SYNTHESIS OF *p*-PHENYLENE VINYLENE DENDRONS & THEIR FUNCTIONALIZATION AND TESTING IN DYE-SENSITIZED SOLAR CELLS

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The novel synthesis of *p*-phenylene vinylene dendrons utilizing a Horner-Wadsworth-Emmons based approach is described. The extended, linear π conjugation along all the dendron branches, a feature absent in most dendrimers used for light harvesting, was expected to lead to an efficient light-harvesting system by acting as a dendritic molecular wire between peripheral donor chromophores and a core acceptor. To that end, nickel porphyrins were added to the periphery of the dendrons as preparation for inclusion in dye-sensitized solar cells. The prepared dendron-porphyrin conjugates proved to be poor dyes. This disappointing result is attributed to the use of nickel porphyrins which were found to undergo non-radiative decay, making them unsuitable for light-harvesting applications. Changes to the system are proposed, from replacing the nickel with zinc within the porphyrins to the use of alternative chromophores, to better test the dendrons function as molecular wires.

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ACKNOWLEDGMENTS

I'm done at last! However, I would not have made it to this point without the help and support of so many others. I'd like to think they all know how important they were to me in reaching this point, but I'd like to acknowledge some here so that everyone else may recognize the parts these others played.

First, I have the best family ever. Mom and Dad, thank you for being awesome. For the unconditional support, which I know is kind of a given being your son, but whenever things didn't go as planned, it made all the difference in giving me the chance to recalibrate and get going again. For all the phone calls listening to me describe what I was working on, and what wasn't working, and for being genuinely curious about it all and letting me share that with you. And for the visits to Pittsburgh when you reminded me of balance and we did stuff other than chemistry from Pirates games to geocaching to exploring all around Pittsburgh. There's still so much to do too! Mike (and now Vanessa too), thanks for always being just as awesome (aren't Mom and Dad great, we turned out better than expected, eh?) and for all the support and encouragement from you as well. To each of you, I love you.

Thank you to all my friends who have offered a kick in the ass when needed (and sometimes when not) and been cheerleaders the rest of the time. To Emily Conant who has put

up with me the most and for almost the entire time I was here at Pitt. The stress of school and life has intruded a bit too often, but when that has been placed aside you have been there mostly cheering me on to the finish of this, even if it wasn't completely altruistic. Finishing up so I have time to come roam the mountain west and go hiking in Glacier, Yellowstone and Yosemite with you sounds pretty good. Even checking out and being a wildlife technician monitoring your speed goats while you make your way through grad school now would be pretty fantastic. Perhaps those are why you were pushing me to get done, but those are acceptable reasons in my book. Thanks for all the good times.

A special thanks to Sam Zolin and Sarah Sears who have been there especially the last three years which were especially stressful. It was as if an occult hand guided you two to each other, and then Sam to register for honors organic lab where I was treated to his quips…or maybe it was just George. From student, to co-teacher, to friend and now taco and burrito connoisseurs eating Qdoba fit for the aristocracy, your irreverent sense of humor has been the perfect complement to your encouragement to "hurry up and finish."

Speaking of George, that would be none other than George Bandik, a former member of the Chapman group himself. It is not an understatement to say, "Without George, I'd be (insert doing something other than finishing grad school here)." When I chose to leave the first research group I'd joined, I considered leaving Pitt as well. I knew I wanted to teach though, and George helped me navigate the process of finding a new research advisor and in finding one who would also help me reach that goal. I could not list all the things that George has been of help with. I am thankful for the years coordinating the organic chemistry lab program and teaching the honors organic chemistry lab with him. I doubt there is anyone else who better understands what this journey has been like for me. Of course, I can't mention George without thanking his boss,

Regina Mahouski. During some of the most anxious months this last year, Regina was the break from writing. I first met her while coordinating labs with George. All too soon she learned my tendencies so well that she coined a nickname I've gone by ever since. Thank you for all the laughs, all the help, and all the support.

And a final thank you to former students of mine, so many of which I now consider friends. It is because of you that I enjoy teaching so much. It is because of your belief in me that I always kept pushing to finish because I had to get that opportunity to teach. I think there was no greater motivator for me than to know I needed this PhD so that I could keep teaching the rest of my life. You're all fantastic. I worry about naming any of you in particular because I'll surely remember more to add once this has already been submitted. I will give a nod to Jordan Deaner, Matt DiLucia, Geoff Eddinger, and Akira Shimizu. I hesitate to name more of you because this would become longer than the science I write about later and I know I've already left some out. You all know what role you've played. If you're ever around, consider being left out here an invitation to lunch. Let's catch up!

* * * * *

Of course, completing this dissertation required a lot of chemistry to be done as well (who'd have guessed!), and that would not have been possible without the wonderful guidance of Toby Chapman. The first time we met was to discuss possible research projects. After finishing with those which were already started, he decided to share his idea to "save the world." Of course that was the project I was interested in even though it was a brand new project with no work completed on it yet. So thanks first and foremost for letting me work on the project I wanted and in which I had interest. Thanks for always having an open door to come by and discuss results or new directions to take the research. I only wish I'd had more of the real whiz-

bang-yippee type results to share. Those are much rarer than others though, I suppose that's why they're so exciting. Thanks for being allowing me to explore chemistry in the lab and to continue to explore life outside of it. Thanks for the opportunity and encouragement to pursue teaching and to find that mix of teaching and research that worked for me.

Of course, Dr. Chapman is a strong believer in undergraduate research as well. Thanks to each of the almost 25 undergraduates I had to opportunity to mentor. While working with you all added years to my degree, you all added much more to who I am as I finish this phase, ultimately helping to guide me in my next steps towards teaching chemistry for the rest of my life. My undergraduate research experiences helped me to decide to go to grad school. I hope the time we shared in lab was as valuable to you. Special thanks to Rock Mancini and James Apgar for being outstanding.

I also must acknowledge Bo Ding and Kristy Gogick. Bo was my solar cell expert. Shortly after we began our collaboration with Dr. Lee's group with the goal of preparing dye-sensitized solar cells we were introduced to Bo. While completing his own PhD this year, Bo also prepared and tested the dyes I prepared. And when they were more than disappointing, and I still needed measurements from all three dyes, Bo was there to make the cells and test them, just to help me collect a few more data points. Thank you Bo for being so helpful. I wish I could have come over and helped out, but we never did meet up on that. I still want to make some solar cells my self! Kristy was my latest contact for help collecting UV-Vis & fluorescence data. While I spent most of my time with organic synthesis, the trips down to collect this data were always a bit out of my comfort range. Thanks for sharing time on the instruments, and helping me collect all the right data. I wasn't sure I needed so much fluorescence data as we collected. It was far more than I'd ever collected for the dendrons. All

that data though proved key to understanding how my dyes were functioning (or not really functioning as it turned out.) I give a tip of the hat to you and Michelle Muscatello too for the helpful discussions in interpreting all that data and pointing me in the right direction so that I was able to eventually figure out what was happening.

Also helpful in collecting all the data necessary to characterize the new compounds synthesized in this project were Sage Bowser & Damodaran Krishnan with the NMR facility. Thank you to Bhaskar Godugu and his predecessors and assistants in the mass spectrometry facility. Thanks especially for the patience in searching for a way to gather mass data for my dyes that we never did find. Thanks also to Steve Geib for his help with collecting all the x-ray crystallography data and understanding it, and providing the files in so many formats until I found the ones that worked with software I had. Without all of you, the data needed to carry out the basic research being done here would never get collected.

I could also have never completed my research without the help of all the chemistry department staff. So often the only times I'd stop by were when I needed something, an account number, a missing shipment, some random paperwork, or a request for something to be fixed. You keep this place functioning, no small feat with the egos that seem par for the course that all coexist in this setting that all expect they're most important. I don't know what I'd do without you. I never considered anything all that urgent that it needed immediate attention, and yet so often that's just what I got. Thank you!

And lastly, thank you to Tara Meyer, David Waldeck, Jung-Kun Lee and Christian Schafmeister who have all served on committees of mine over my time here. I never did shake the anxiety I felt during meetings with you. Still, I always left with new ideas for the work and new ways to tackle problems I was encountering. Your interest in making sure the students all

have the best chance to succeed is one of the reasons I chose Pitt. Thank you for all of your help in my success.

Finally, I could not have finished this work without the help of Jay Auses. I mean that literally. I try my best to live with no regrets, however if I were to have one, I wish I'd approached you sooner to help me work through the things we first resolved. I had been given no indication that clearing those obstacles was possible. Thank you! You played an integral part in my finally wrapping this up. I simply don't have the words.

* * * * *

Looking back on my path to this science point in life, I could probably trace all the way back to waking up first in the house to watch Don Herbert as Mr. Wizard on Nickelodeon at some early hour. My parents certainly encouraged my brother and I all along. I remember recreating simple experiments I saw on that show in our kitchen. More directly related to chemistry though, I owe thanks to my high school chemistry teacher, Mary Short at South Bend Clay High School in Indiana. Following chemistry classes my sophomore and junior year with her, I was fortunate that my good friend's father was a chemistry professor at Notre Dame. And so the summer before my senior year of high school I got my start in a research lab with Dr. Paul Helquist. Little did I know that would lead to me then teaching the organic chemistry labs that fall an experiment I'd developed that summer. And from there it almost seems I was predestined to reach this point. Teaching organic chemistry when I was 17. I didn't know what I was doing! I wasn't even considering applying to Notre Dame. A year later though I was enrolled there and pretty sure I would study chemistry. The last three years I continued research with Dr. Helquist and Dr. Olaf Wiest who had been my organic chemistry professor. As that all came to an end, it was little surprise to me that I was interested in becoming a professor of organic chemistry with

my own research lab just like them. That's changed just a bit as I have realized just how much I love teaching, but the path they guided me on has reached yet another milestone, and I owe so much to their influence.

* * * * *

Finally, I include here the placeholder that I never intended to be in the final form of this document, but it doesn't seem right to exclude it now. It is a quote I inserted just to make me smile when I opened the drafts and to make sure I didn't delete the page where these acknowledgments were to be inserted. Recently I've become reacquainted with Doctor Who which I occasionally watched as a kid. While my favorite Doctor is the Tenth, one of his successor's oft repeated lines seemed perfectly suited to this:

> "These are *p*-phenylene vinylene dendrons. I make *p*-phenylene vinylene dendrons now. *p*-Phenylene vinylene dendrons are cool."
>
> *– The Eleventh Doctor (paraphrased)*

Allons-y!

LIST OF ABBREVIATIONS

ATP	adenosine triphosphate
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
BINOL	1,1'-bi-2-naphthol
bpy	2,2’-bipyridine
cm	centimeter
conc.	concentration
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DMF	*N,N*-dimethylformamide
DSSC	dye-sensitized solar cell
eq	equivalents
FRET	fluorescence resonance energy transfer
g	gram
HOMO	highest occupied molecular orbital
HRMS	high-resolution mass spectrometry
Hz	Hertz

imid	imidazole
IR	infrared
KO*t*Bu	potassium *tert*-butoxide
L	liter
LED	light-emitting diode
LH1	light harvesting complex I
LH2	light harvesting complex II
LUMO	lowest unoccupied molecular orbital
M	molar
MALDI	matrix-assisted laser desorption/ionization
mL	milliliter
mmol	millimole
mol	mole
MsCl	methanesulfonyl chloride
n-Bu	*n*-butyl
nm	nanometer
NMI	naphthalene dicarboxmonoimide
NMR	nuclear magnetic resonance
OPV	oligo(phenylene vinylene)
PAMAM	poly(amido amine)
PDI	perylene tetracarboxdiimide
PhMe	toluene

PMI	perylene dicarboxmonoimide
POPAM	poly(propylene amine)
ppm	parts per million
PSU	photosynthetic unit
RC	reaction center
RT	room temperature
TBS	*tert*-butyldimethylsilyl
TCO	transparent conducting oxide
TDI	terrylene tetracarboxdiimide
TEMPO	2,2,6,6-tetramethylpiperidine 1-oxyl
THF	tetrahydrofuran
TLC	thin-layer chromatography
TsOH	*para*-toluenesulfonic acid
UV	ultraviolet
Vis	visible

1.0 AN INTRODUCTION TO DENDRIMERS

Dendrimers are highly branched, tree-like macromolecules.[1-4] Due to the fashion in which they are synthesized, they are monodisperse with well-defined structures. Buhleier, Wehner, and Vögtle were the first to publish the synthesis of compounds that would later be classified as dendrimers.[5] At the time, the compounds were simply referred to as the products of cascade- or non-skid-chain-like syntheses. The term dendrimer is based on the Greek term *dendros* (tree-like) and *meros* (part of). Donald A. Tomalia et al. first used the term in their report of poly(amidoamines) (PAMAM) which they called starburst dendrimers,[6] though they credit A. J. Vogel for coining the term.[7]

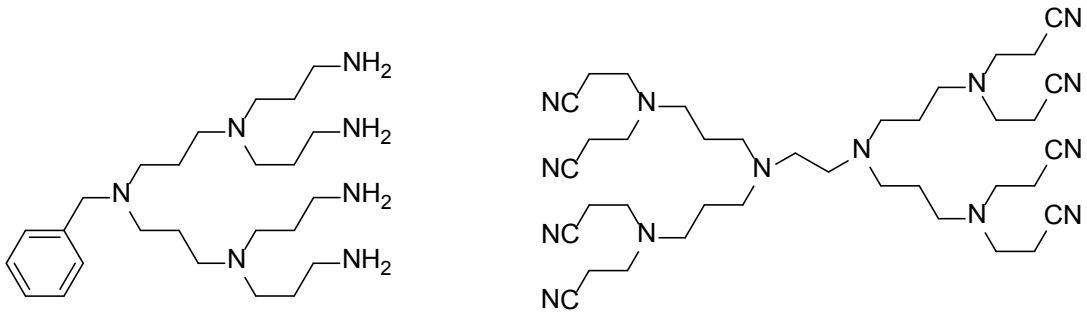


Figure 1.1. In modern terms, a dendron (left) and dendrimer (right) originally reported by Vögtle et al. as cascade molecules in 1978.

1.1 SYNTHESIS

In addition to PAMAM, reports of other dendrimers were sparse early on, highlighted by poly(propyleneamine) (POPAM),[5, 8, 9] and polylysine.[10-12] All of these dendrimers were constructed using a divergent approach. Divergent synthesis of a dendrimer is where the macromolecule is built starting from the eventual core unit. It is functionalized with two or more reactive sites that are coupled with the new branched monomers. These monomers are often masked with some protecting group which will be removed revealing additional reactive sites. The dendrimer is thereby synthesized layer by layer. These layers are called generations. As generations are added, the dendrimer grows from the central core outwards.

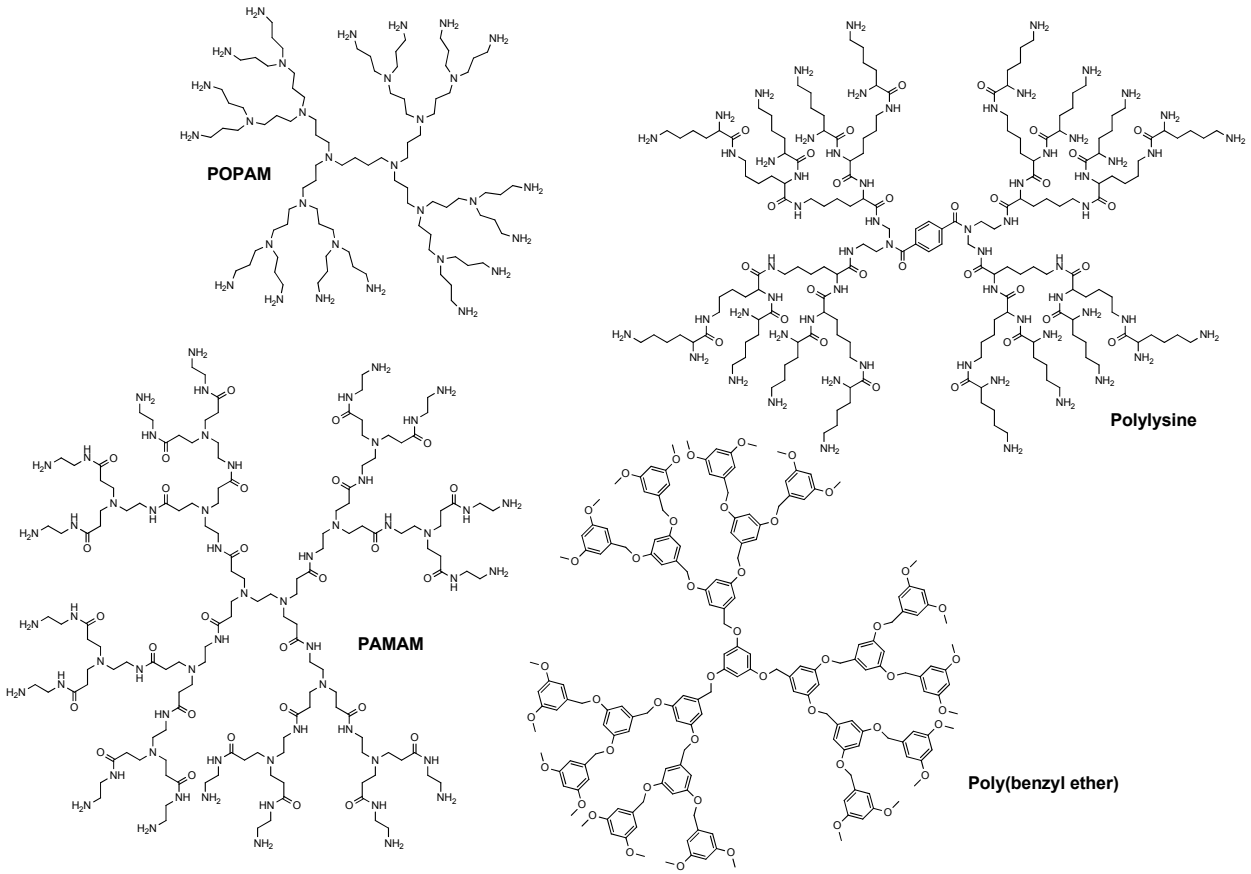


Figure 1.2. Some common dendrimers.

PAMAM and POPAM are manufactured commercially using a divergent synthesis due to the ability to automate the repetitive steps of dendrimer growth and deprotection.[4] The divergent method has several disadvantages though. As the dendrimers are synthesized, the number of terminal reactive sites increases exponentially. In order to realize reaction at each of these sites, large excesses of reagents are used. Even so, in higher generations incomplete reaction becomes an issue. Each unreacted site introduces a structural defect into the dendrimer architecture that will be magnified with each generation until it can be purified. Purification of the defective

dendrimers is made difficult in the divergent method as well though. The properties of the perfectly formed dendrimers and the defective ones are very similar.

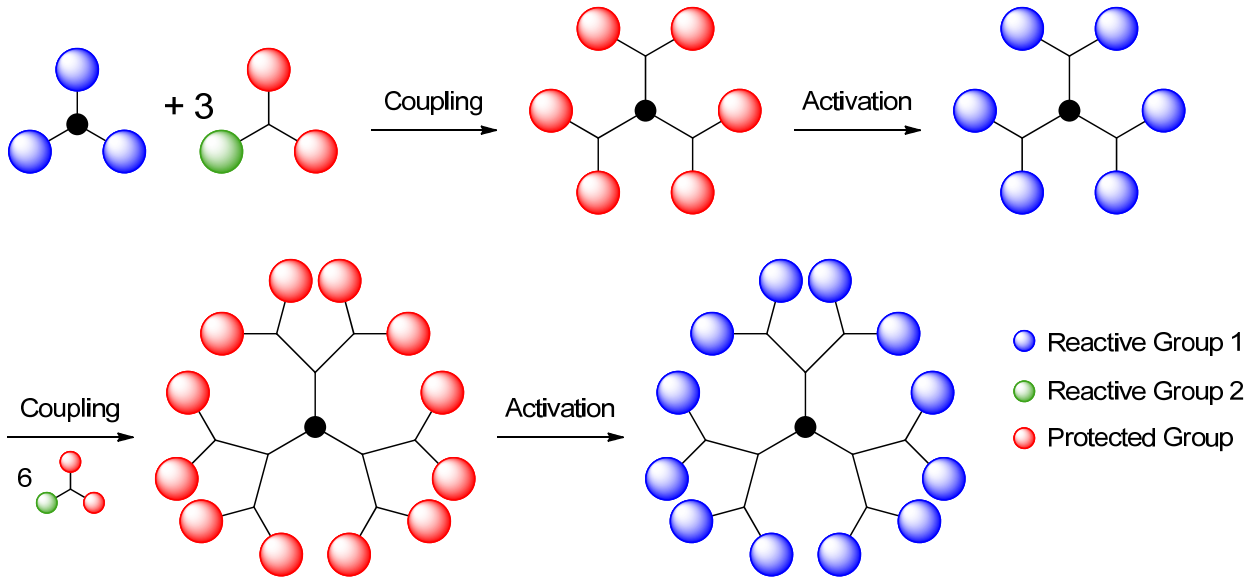


Figure 1.3. Divergent synthesis of a dendrimer.

In 1990 a new convergent method for dendrimer synthesis was introduced by Hawker & Fréchet.[13] This method builds the dendrimer structure starting from the outside. Hawker demonstrated this new synthetic scheme making a poly(benzyl ether) dendrimer based on 3,5-dihydroxybenzyl alcohol. The structures built in this fashion are referred to a dendrons. In the last step, two or more dendrons are attached to a central core unit to yield the final dendrimer.

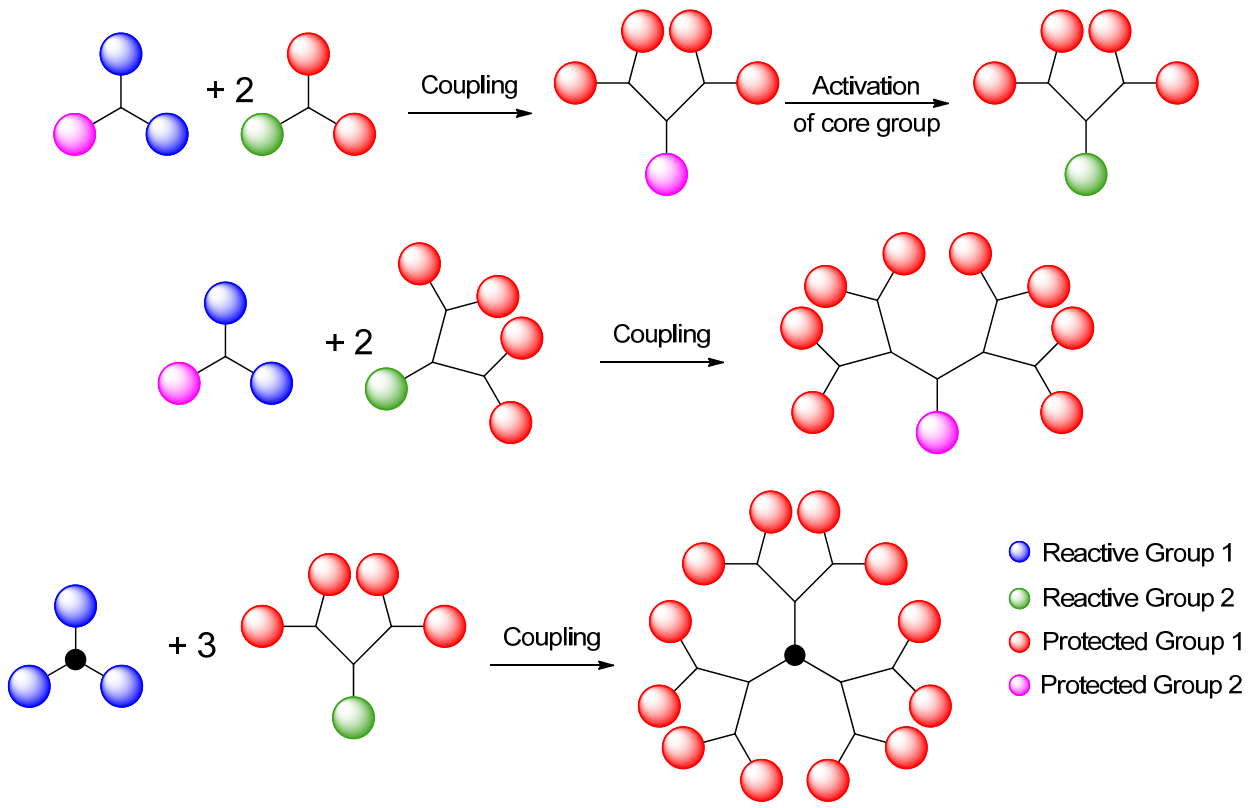


Figure 1.4. Convergent synthesis of a dendrimer.

This approach has several advantages, primary among them that the convergent method does not lead to structural defects. In building each successive generation of the dendrons, a small number of reactive sites are involved. This number is constant, rather than growing exponentially with successive generations. This leads to other advantages as well. Large excesses of reagents are not necessary with this method. Also, the properties of the products of incomplete reaction versus complete reaction are very different. This means purification of the products is easier and any defective dendrons can be removed after each step, a difficult task with a divergent synthesis. The convergent method also is useful for controlled substitution of the dendrimer periphery, for example in the synthesis of Janus dendrimers.[14]

The convergent method does have some disadvantages though. As the dendrons become larger, steric hinderance places limitations on the possibility of higher generations. Therefore, this method is often employed mainly for the preparation of lower-generation dendrimers.

1.2 THE NATURAL PHOTOSYNTHETIC UNIT

Dendrimers are used or have been investigated for use in a number of areas. These include being used in catalysis, pigments and inks, LEDs, various medical applications, and light-harvesting.[4] Light harvesting has drawn particularly high interest due to an unavoidable comparison to the natural light harvesting complexes found in photosynthetic organisms.

Much of the life on Earth uses energy that is derived from sunlight whether it is directly as in the case of plants or photosynthetic bacteria or indirectly by organisms higher up the food chain.[15, 16] The plants and bacteria that directly harvest sunlight for energy have developed complex and highly efficient systems to carry out this function. The structure of the photosynthetic reacton center was determined by Johann Diesenhofer, Robert Huber, and Hartmut Michel.[17] For this work they were awarded the Nobel Prize in Chemistry in 1988.

The biological photosynthetic unit has the same basic structure and function whether investigated in photosynthetic bacteria[17-28] or plants.[29, 30] Chromophores are arranged in a manner so that once they have absorbed light, the captured energy is quickly and efficiently funneled to a reaction center where it is used towards production of ATP.

The purple bacterial photosynthetic unit was the first to be solved by Diesenhofer, Huber, and Michel. It is comprised of three main pieces: the reaction center (RC) and two antenna complexes responsible for light-harvesting, LH1 and LH2. The antenna complexes are

comprised of a circular array of chlorophylls or other chromophores coordinated with the peptide chains to hold them in a well-defined location and orientation. The primary difference is in size. LH2 is smaller and contains fewer light harvesting molecules. LH1 is larger with more chromophores and encircles the reaction center. The number of chromophores in LH1 and LH2 is not constant though and varies from species to species.

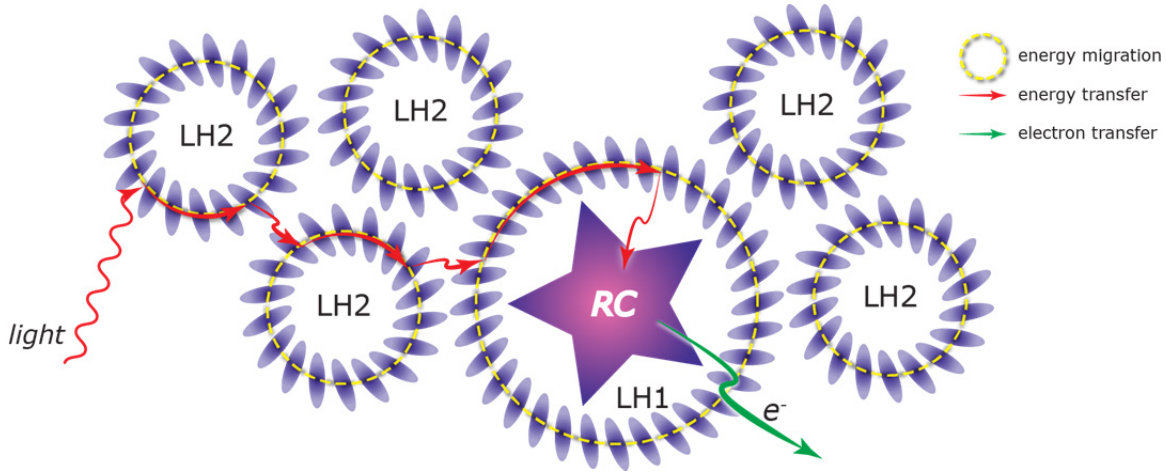


Figure 1.5. Representation of the purple bacteria photosynthetic unit.

When a photon is absorbed, because of the precise arrangement of the chromophores, that energy is shuttled around the LH2 complex with very high efficiency before being passed off to another antenna complex,either LH1 or possible a second LH2 depending on where in the entire photosynthetic unit the energy was absorbed. Once funneled to the LH1 complex, the energy is finally delivered to the RC. This transfer occurs very efficiently with approximately 95% quantum yield and extremely quickly in under 100 ps.[31, 32]

1.3 FUNCTIONALIZATION OF DENDRITIC STRUCTURES

Dendrimer structures are immediately reminiscent of the natural photosynthetic unit. Their highly branched structure has many locations at which chromophores could be associated around a central core unit. This was recognized early on, as interest in dendrimers and elucidation of the photosynthetic unit were simultaneous endeavors. As reports of dendrimers in the literature increased, so did reviews on their potential in artificial photosynthetic devices.[33-45]

In order to better distinguish types of functional dendrimers, such as those investigated for light-harvesting, it is helpful to categorize them. This is easily done by sorting them based on the manner in which they are functionalized. Three main types of modifications are found. Dendrimers with functional units at their core. Dendrimers which have functional units attached to the periphery. And lastly, dendrimers which have functional units within their structure forming a host-guest complex. Of course, multi-functional dendrimers can be synthesized utilizing multiple functional units among these different locations.

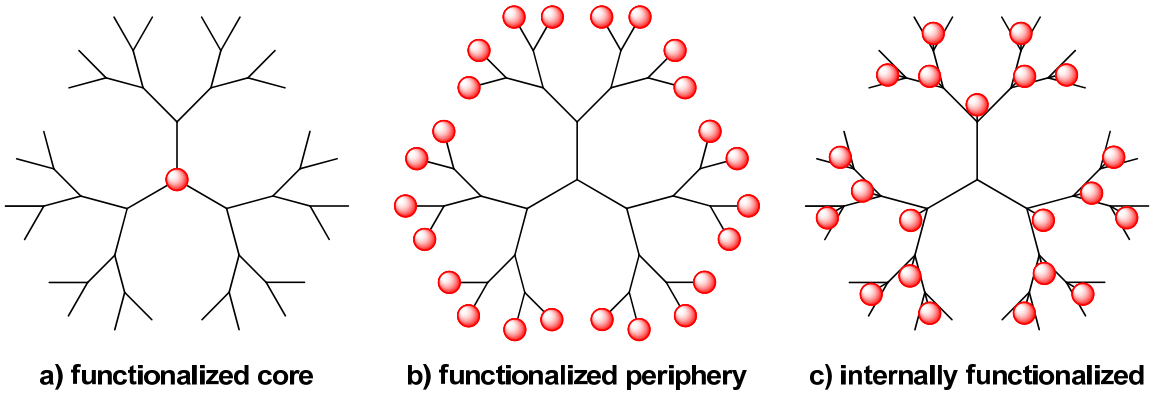


Figure 1.6. Three common modifications to add function to dendrimers.

1.4 LIGHT-HARVESTING DENDRIMERS

In efforts to mimic the natural photosynthetic unit, dendrimers have been synthesized utilizing combinations of these approaches. To mimic the array of chlorophyll and other light harvesting molecules in the photosynthetic unit, many dendrimers have been decorated with chromophores around their periphery. Energy absorbed by these chromophores is then transferred to the core of the structure. In other cases, the dendrimers themselves are the chromophores. Energy absorbed by the dendron branches is transferred to a central point in the structure. Some examples of systems that have been studied for their light-harvesting abilities are reviewed below.

1.4.1 Dendrimers that absorb via attached chromophores

The most popular system for studying light-harvesting in dendrimers involves functionalization of the periphery (see Figure 1.6b**)** of the dendrimer with strongly absorbing moieties. This affords the opportunity for researchers to match the donor and acceptor chromophore's properties to best observe excitation energy transfer. The central acceptor can be one of several things from a second organic chromophore attached at the focus of the dendrimer (see Figure 1.6a**)** to an acceptor present within the dendrimer framework in a host/guest situation.

1.4.1.1 Transfer to a core organic chromophore

The most widely reported system for light-harvesting involves functionalization of the periphery of the dendrimers with one chromophore and of the core of the dendrimers with a second.[37, 46-54] Among the earlier reports of light-harvesting in dendrimers, Fréchet and

coworkers decorated the benzyl ether dendrons developed in their lab with coumarin dyes as shown in Figure 1.6. Coumarin 2 was attached to the periphery. At the focal point, a single coumarin 343 moiety was placed, chosen for the overlap of its absorption band with the emission band of coumarin 2. Generations 1 through 4 therefore had 2, 4, 8, or 16 coumarin-2 donors respectively per coumarin 343. Energy transfer efficiencies of 97% and up were found for the first three generations. Generation 4 exhibited a fall in efficiency to 93% attributed to the increasing distance between the two units resulting in less effective fluorescence quenching by the coumarin 343.[47, 52] Fréchet dendrons are used by others as well owing to their absorption being completely below 300 nm, simplifying interpretation of the energy transfer processes when the chromophores are chosen that absorb above this threshold.[53]

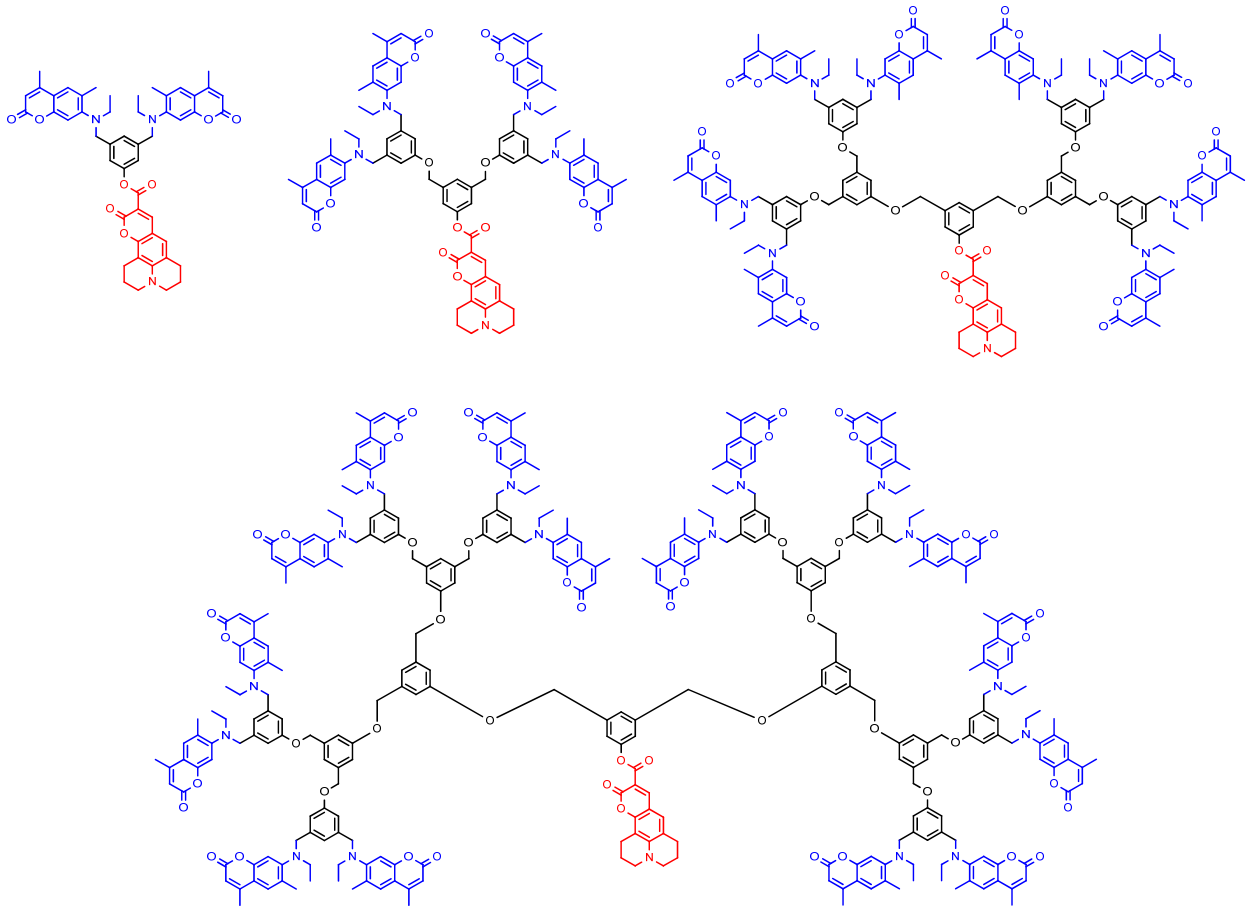


Figure 1.7. Structures of G1 thru G4 coumarin-decorated Fréchet benzyl ether dendrons.[52] blue = coumarin 2, red = coumarin 343

Another example of dendrimers which transfer energy absorbed by chromophores at the periphery to a central point are multiporphyrin arrays.[37, 48-50] In one report up to 29 porphyrins were arranged in a dendrimer with zinc porphyrins placed around a core free base porphyrin. Of note was that only when four porphyrin dendrons were placed around the free base porphyrin was highly efficient energy transfer achieved. The authors propose that this increase in efficiency was due to the shell porphyrins acting cooperatively prior to energy transfer to the

core, similar to the means by which energy is harvested by a shell of chromophores in the natural photosynthetic system.

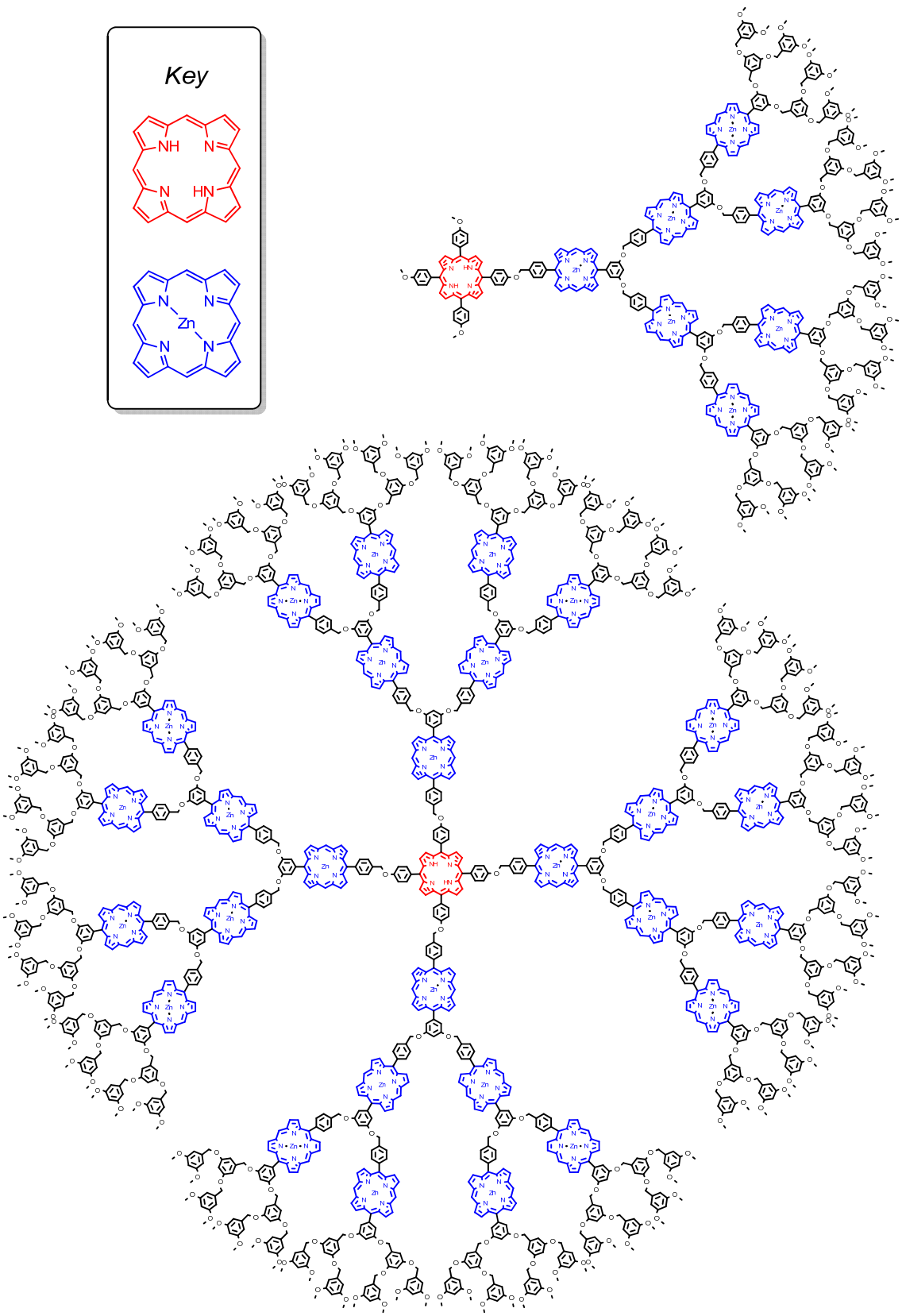


Figure 1.8. Light-harvesting multiporphyrin arrays by Aida et al.[49]

1.4.1.2 Transfer to a core metallic chromophore

The core organic chromophore can be replaced by a metal complex. Shown in figure 1.9 are a pair of Ru^{II} complexes with bipyridine ligands that have been dendronized with the addition of Fréchet benzyl ether dendrons. Coumarin 2 or naphthalene is used as the chromophore placed at the dendron chain ends. These absorb the energy and transfer it via FRET matching the emission of the coumarin 2 or naphthalene to the $[Ru(bpy)_3]^{2+}$ absorption. 90-95% of the emission is quenched by the ruthenium core.[55, 56]

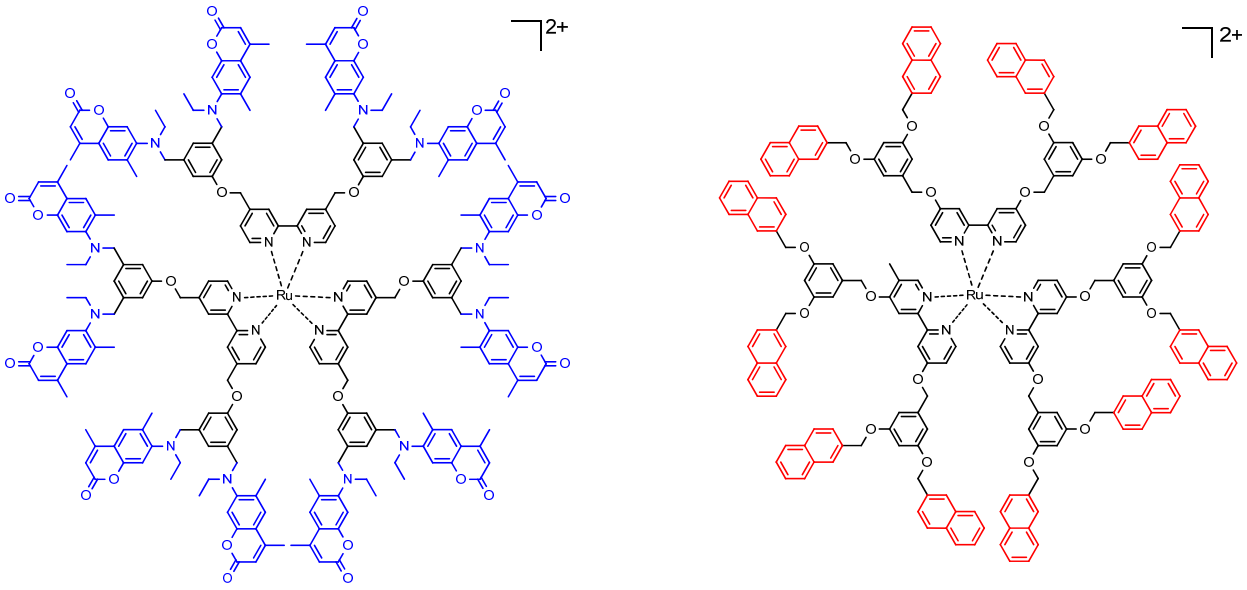


Figure 1.9. Light harvesting dendrimers with metallic $[Ru(bpy)_3]^{2+}$ based cores.

1.4.1.3 Transfer to a guest chromophore

It is not necessary for the energy acceptor to be bonded and present as the core of the dendrimer. In 2000, Balzani et al.[57] and Schenning, Peeters, and Meijer[58] independently reported

examples of light harvesting dendrimers in which the acceptor entity was a guest within the host POPAM dendrimer.

Balzani et al. utilized the fourth generation POPAM dendrimer with 32 dansyl units on the periphery as donor chromophores in Figure 1.10. Eosin was introduced as a guest into the dendrimer framework. Upon selective excitation of the dansyl groups at 370 nm, the eosin fluoresced strongly. Comparisons were made to a solution containing the dendrimer and the eosin, but not incorporated as a guest. The fluorescence quantum yield more than doubles when the eosin is included within the dendrimer framework.[57, 59]

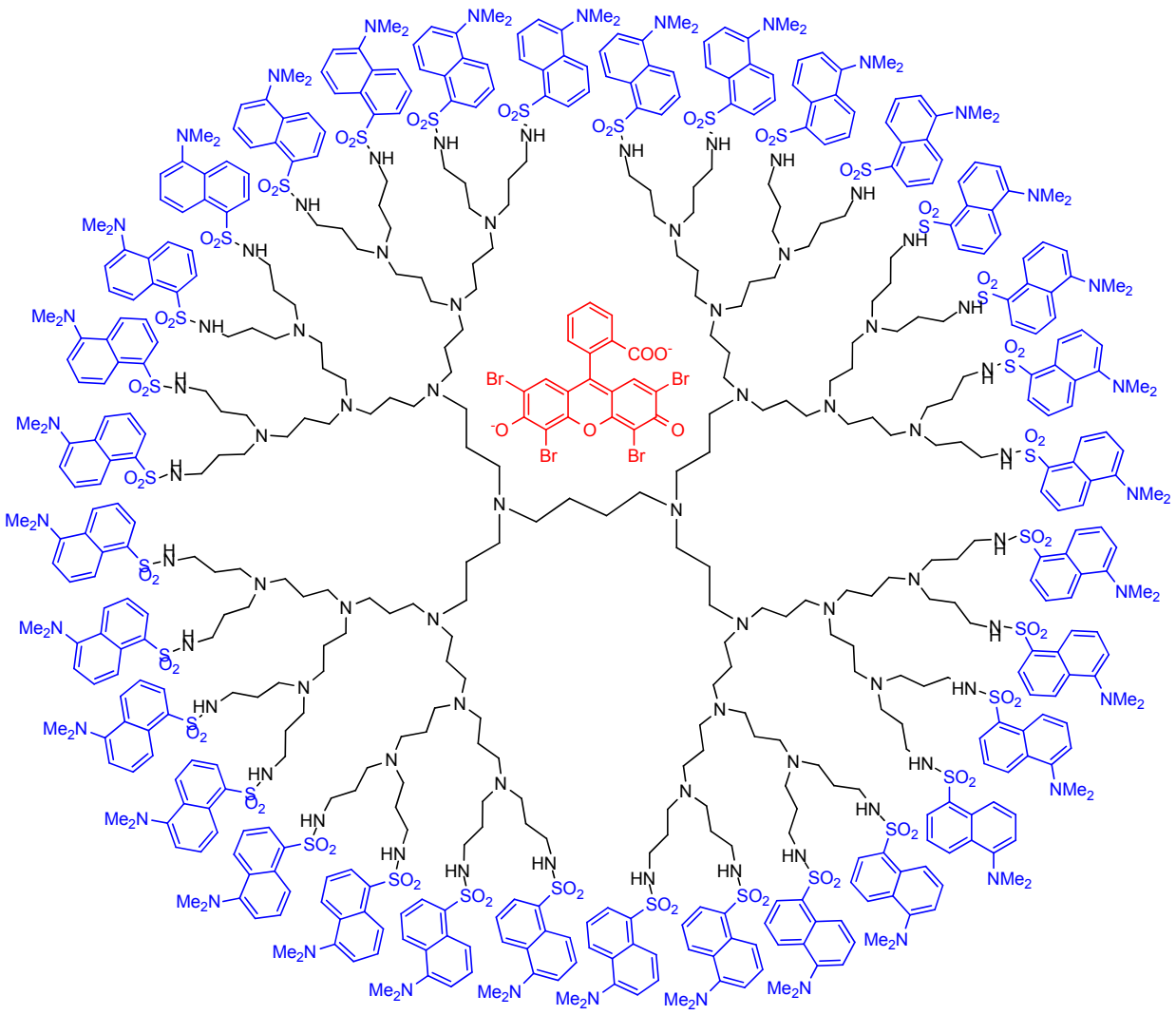


Figure 1.10. Example of light harvesting POPAM dendrimer with 32 pendant dansyl donor chromophores and eosin acceptor as a guest shown within the dendrimer structure.

Polylysine dendrimers make especially good hosts for lanthanide ions due to the numerous amide groups. Dansyl groups were once again featured as the donor chromophores on the periphery. It was found that a single Nd^{3+} or Eu^{3+} ion, the most efficient of the metals tested, could quench approximately 24 dansyl units when incorporated in the polylysine dendrimers in Figure 1.11.[60]

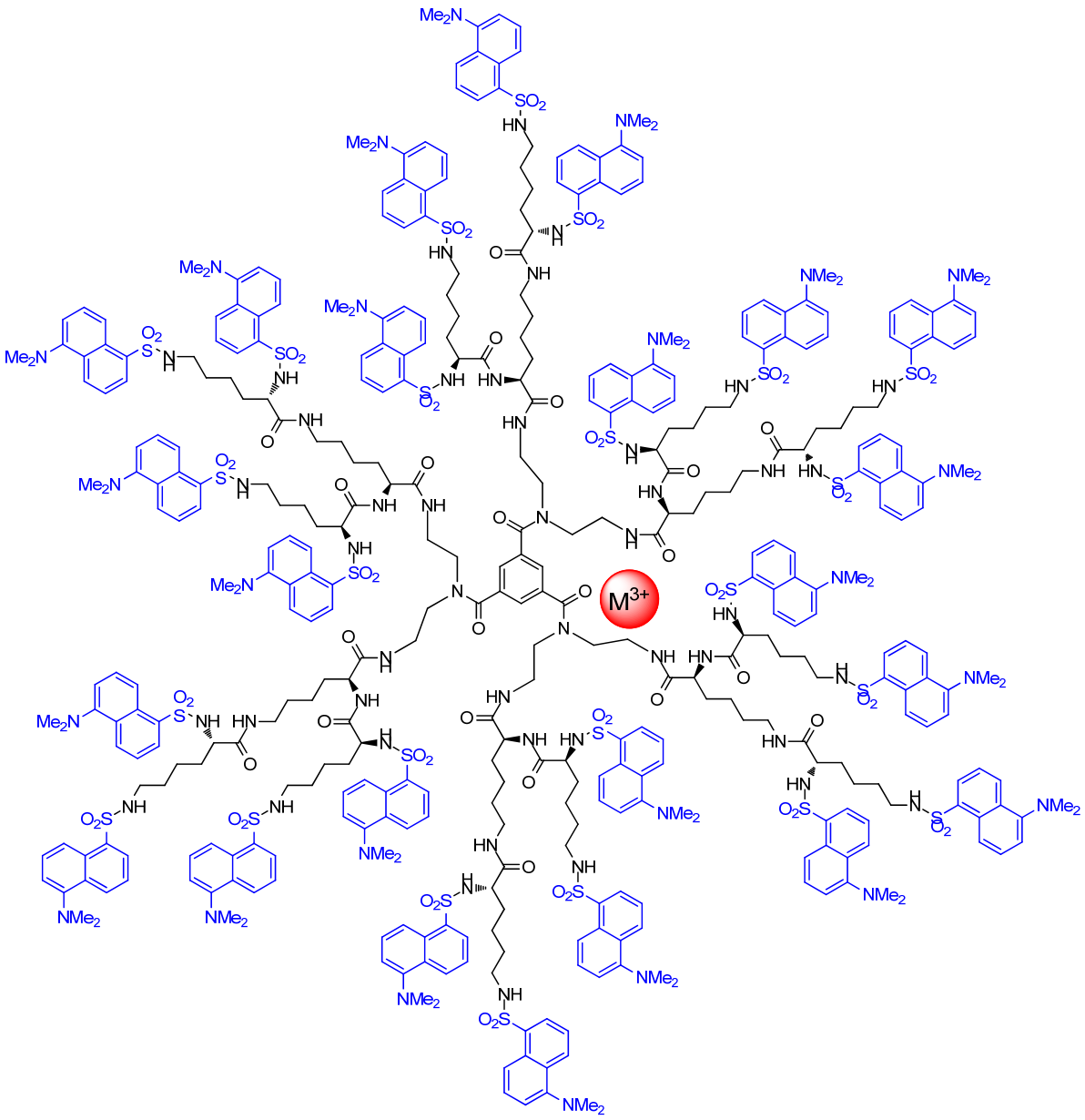


Figure 1.11. Second generation polylysine dendrimer with 24 dansyl donor chromophores. Red sphere representative of lanthanide ion complexed within the dendrimer.

1.4.1.4 Transfer via an intermediate interior chromophore

Multi-step transfer from periphery to intermediate to core

Some especially ambitious examples use dendrimers as a scaffold to which multiple chromophores are affixed. The chromophores are chosen and arranged so as to install an energy gradient from periphery to core of the dendrimer. An outer shell of donors is first excited. Energy is transferred to an acceptor placed on the dendritic framework intermediate to the periphery and core. In a final step, the transfer to the core is completed.[61-66]

Fréchet and coworkers used a combination of coumarin 2, fluorol 7GA, and perylene tetracarboxdiimide (PDI) decorated on benzyl ether dendrons to demonstrate multi-step energy transfer as shown in Figure 1.12. Excitation of the coumarin 2 (λ_{max} = 342 nm) resulted in a 6.9 fold increase in emission from the core versus direct excitation of the PDI core (λ_{max} = 555 nm). Furthermore, the mechanism of transfer via the fluorol 7GA was demonstrated by preparation of dendrimers identical except for the absence of fluorol 7GA. Energy transfer efficiency fell from over 95% to only 79%. This demonstrates the importance of matching donors and acceptors for optimal excitation energy transfer. By their measurements, coumarin transferred 98% of the energy it absorbed to the fluorol which in turn transferred 97% to the PDI core.[61]

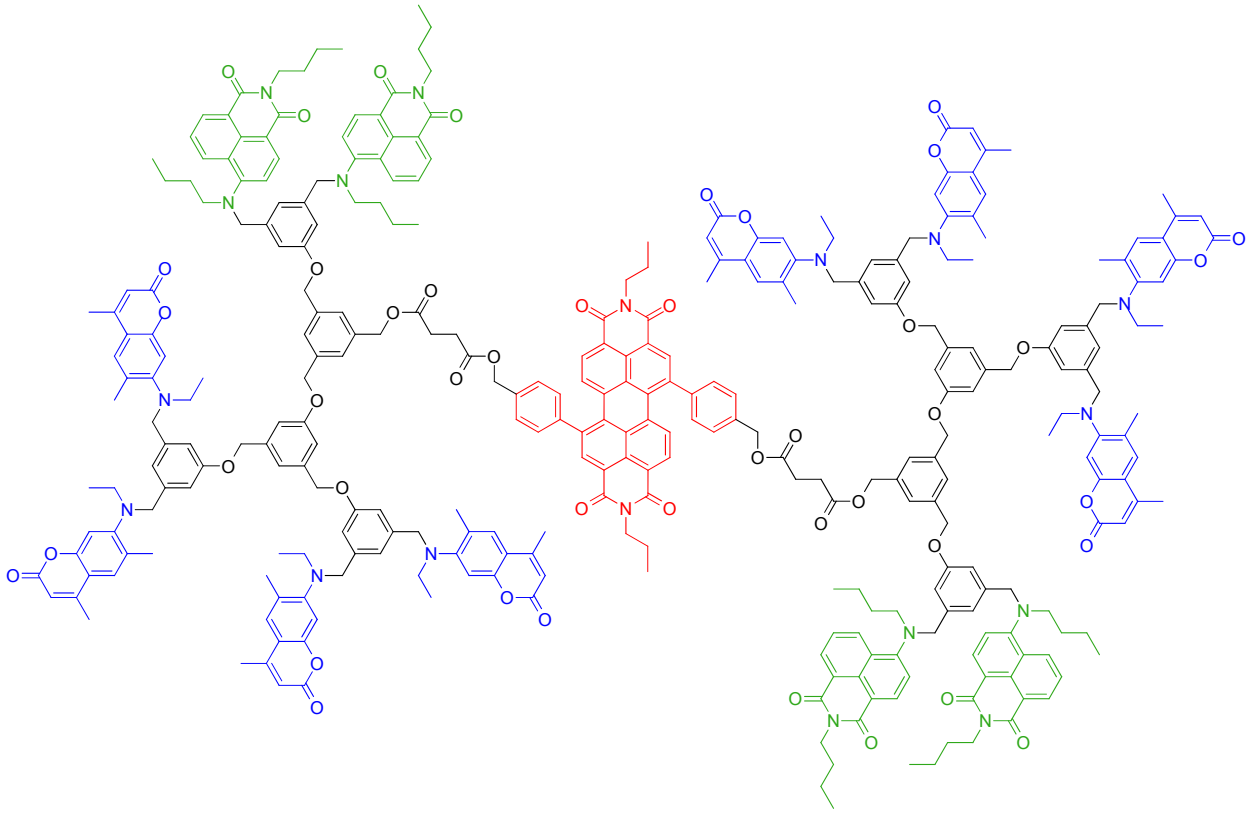


Figure 1.12. 3-chromophore light-harvesting dendrimer consisting of coumarin 2 (blue), fluorol 7GA (green) and PDI (red) arranged around benzyl ether dendrons.

Müllen and coworkers constructed a system in which the periphery chromophore emission and core chromophore absorption did not overlap at all. Their chosen scaffold dendrimer was polyphenylene, shown in Figure 1.13. The nature of this dendrimer provided an additional benefit due to its inflexibility allowing for characterization of the energy transfer step by step. In addition to the directed energy transfer, the antenna effect of the dendritic structure was reported as emission of the core terrylene tetracarboxdiimide (TDI) was monitored as a function of excitation of the naphthalene dicarboxmonoimide (NMI) or perylene

dicarboxmonoimide (PMI) versus direct excitation of the TDI. Emission intensity increased due to the efficient transfer of energy from the antennae chromophores to the core.[62-64, 67, 68]

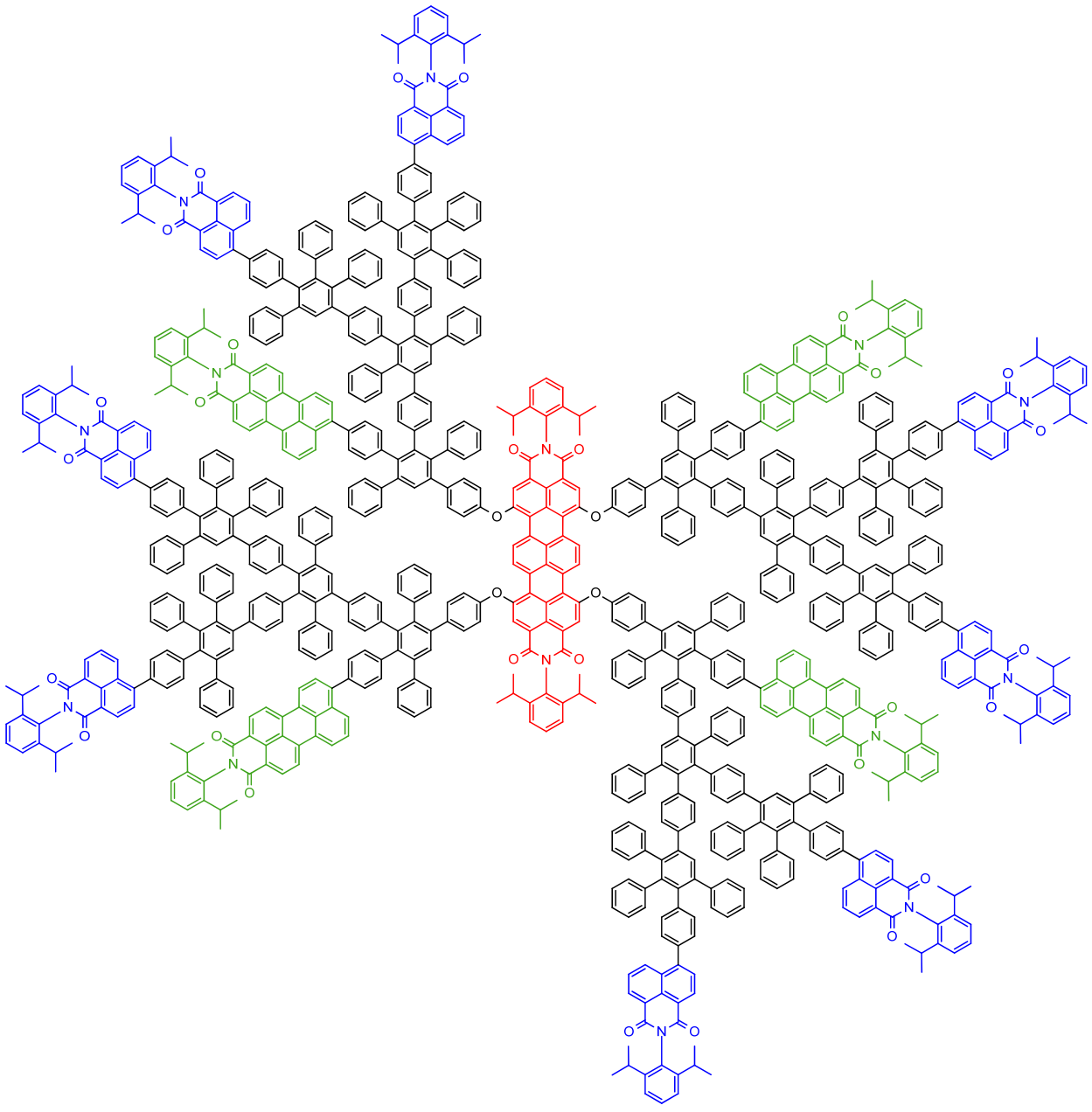


Figure 1.13. Light harvesting dendrimer of Müllen and coworkers designed as so absorbed energy would cascade from the NMI (blue) to PMI (green) and finally to the TDI core (red).[64]

Multi-step transfer from periphery to intermediate to guest

In a final variation, the light-harvested by the system reported by Balzani, Vögtle et al. was ultimately transferred to an eosin guest within the dendrimer framework. Their dendrimer had a polyamine core, internally functionalized with eight dansyl and 24 dimethoxybenzene units, and a periphery of 32 naphthalene units as shown in Figure 1.14. The emission spectrum of this dendrimer showed a strong band (λ_{em} = 514 nm) attributable to the dansyl groups. Emission from other groups had been quenched almost completely (≥ 95%). The fluorescence maximum of the dimethoxybenzene and naphthalene units of 336 nm matched well with the dansyl group's absorption maximum of 340 nm. The dendrimer was then used as a host to acidic dye molecule eosin. Considering eosin has a strong absorption at 529 nm it was not unexpected when they were able to demonstrate efficient light harvesting by this dendrimer with the energy directed to the eosin guest molecules.[66]

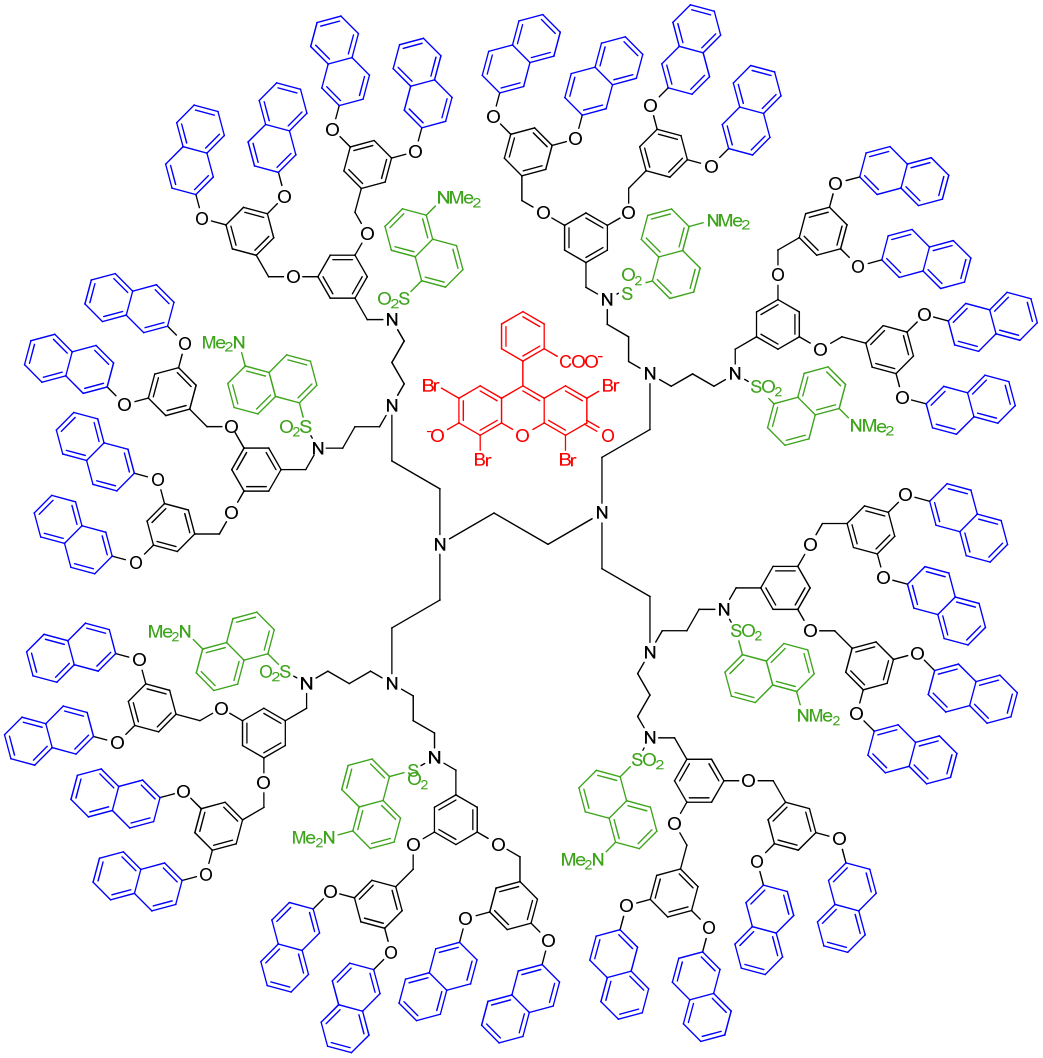


Figure 1.14. A light harvesting dendrimer that transfers energy via cascade to a guest within its branches.

1.4.2 Dendrimers that absorb directly via dendron branches

An alternative to decorating the framework of a dendrimer with absorbing chromophores is to build the dendrimer to absorb light itself. Most, but not all of the dendrimers in this division are comprised of substituted benzene subunits with one or more substituents extending their π

system in order to shift the absorption band to longer wavelengths thus allowing some degree of light-harvesting function.

1.4.2.1 Transfer to a core organic chromophore

Systems in which an organic chromophore has been installed at the core of the dendrimer for the purposes of probing the light-harvesting function are the most studied.[69-78] One of the very first studies of energy transfer in dendritic structures of any type, functionalization with chromophores or by absorption by the dendron branches, was by Moore group which prepared a series a 1,3,5-substituted phenylene ethynylene dendrons asin Figure 1.15.[70, 77-79] By placing a perylene group at the focus of the dendron they were able to observe energy transfer from the dendron branches to the perylene with up to 95% efficiency. However this value fell quickly in higher generations as distance to the perylene increased. The efficiency was increased to 98% in a similar dendron that differed only in the addition of acetylene spacers closer to the core. Because the branches are in cross-conjugation having a 1,3-relationship, the π conjugation does not extend through the benzene rings between branches. Therefore the branches at the periphery are shorter than the shell of branches beneath them, which in turn are shorter than the core branches. This resulted in an energy gradient from periphery to core leading to the high efficiency observed in this case.

The same design motif is present in a series of truxene/oligo (thienylene ethynylene) developed by Pei and coworkers in Figure 1.16. Conjugation does not extend through the truxene branching units. Meanwhile, the branches are longer closer to the core leading to an energy funnel towards the core that yields energy transfer efficiencies of 96%, 97%, 98% for G0, G1, and G2 dendrimers respectively.[76]

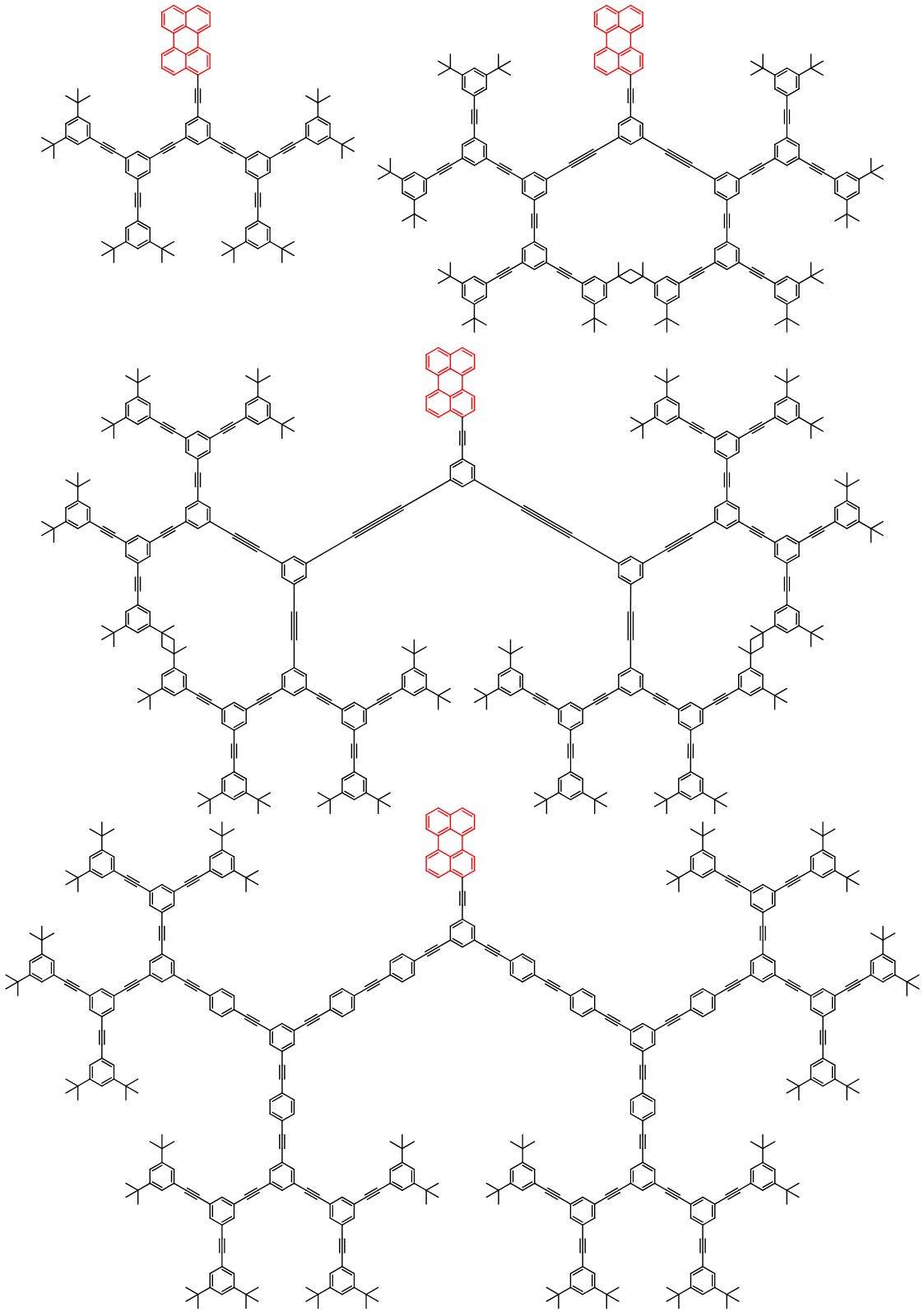


Figure 1.15. Generations 1 through 3 of 1,3,5-substituted phenylene ethynylene dendrons (above) and an example with added spacer groups (below).

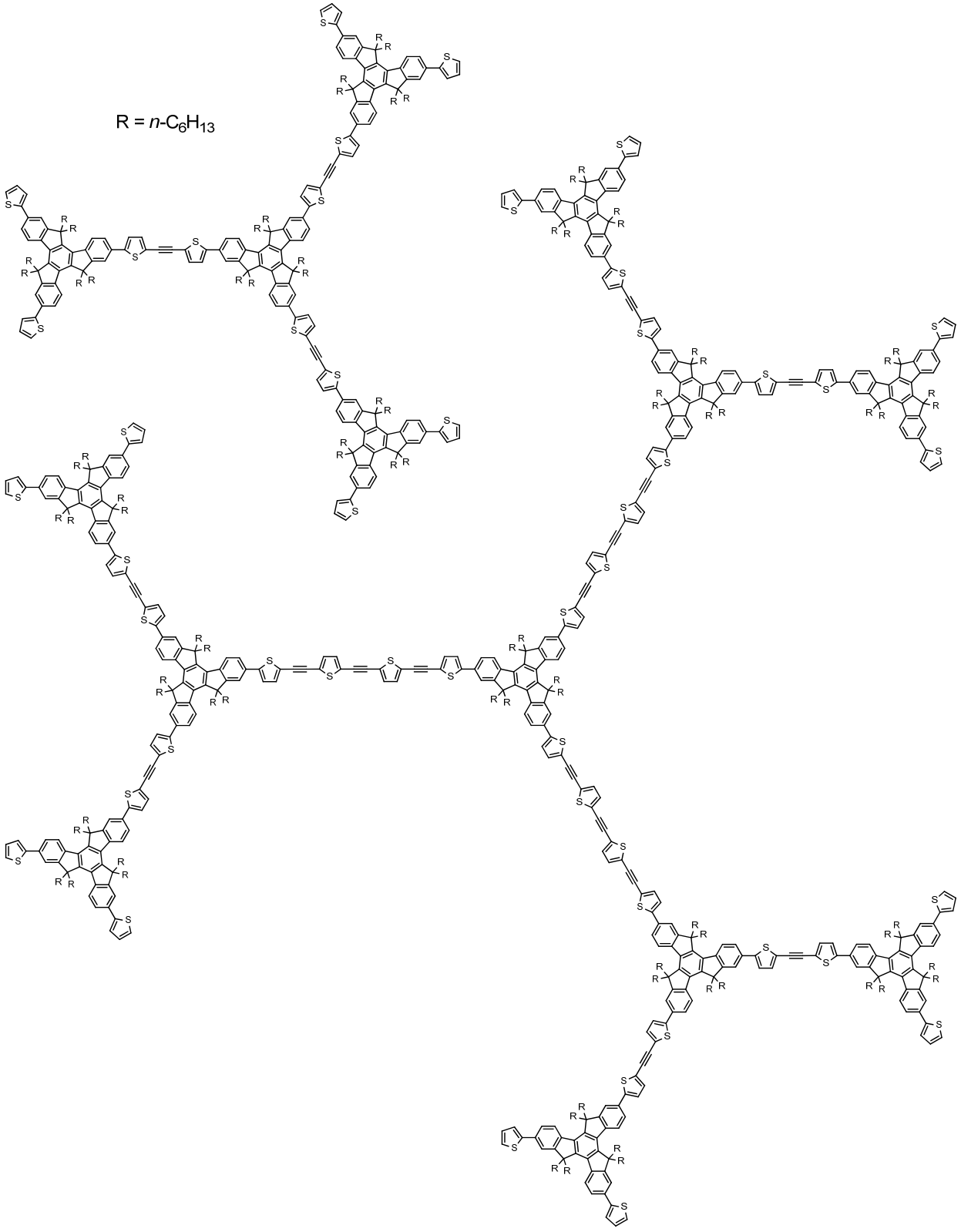


Figure 1.16. Generations 0 and 1 truxene/oligo(thienylene ethynylene) dendrimers of Pei and coworkers.[76]

One other alternative to achieve an energy gradient from periphery to core in order to increase efficiency of energy transfer is to use an unsymmetrically branched dendrimer. 1,3,4-substituted phenylene ethynylene dendrimers have an array of branches of differing lengths of conjugation due to their combination of *meta* and *para* substituted branches. Using a perylene group as energy trap allowed energy transfer efficiencies of 85% an up to be observed in these structures.[72, 74] Nierengarten demonstrated energy transfer from 1,3,4-substituted phenylene ethynylene dendrons to [60]fullerene with the compounds in Figure 1.17. Excitation of the dendrons at their absorption maxima results in dramatic quenching of their fluorescence. Instead a strong fluorescence is observed from the fullerene moiety demonstrating efficient energy transfer from the dendrons.[73]

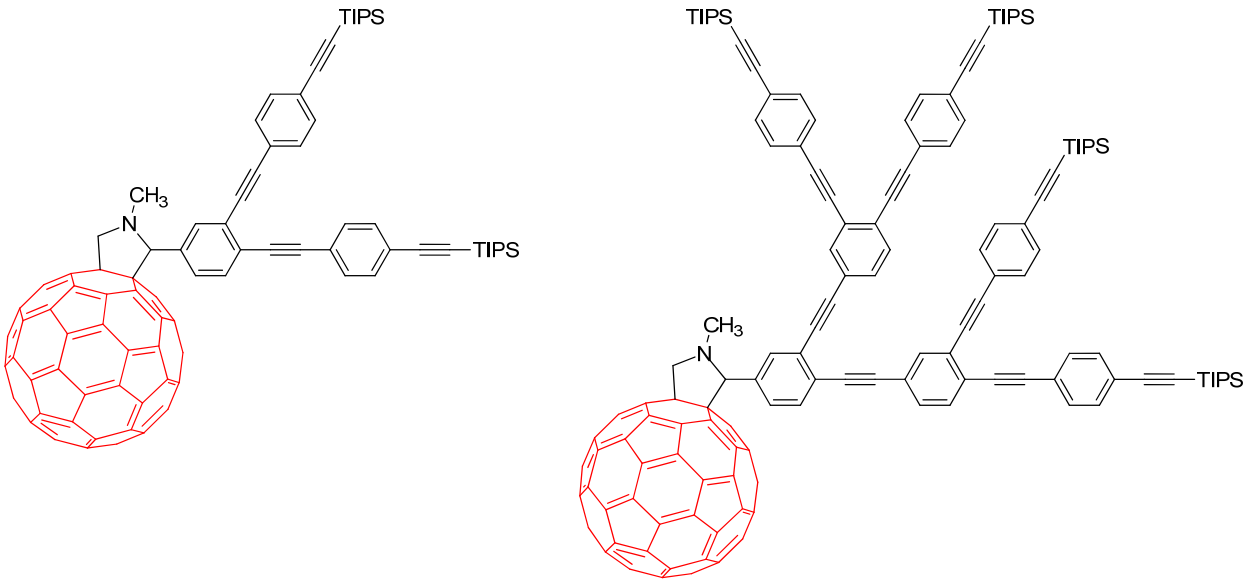


Figure 1.17. 1,3,4-substituted phenylene ethynylene dendrons functionalized with [60]fullerene to observe transfer of energy absorbed by the dendron branches.[73]

It should be noted that light harvesting from dendrons without extended π conjugation has been reported as well. Dendrimers consisting of Fréchet benzyl ether dendrons attached to a porphyrin core[71] or to viologen core[69] have been prepared. With the viologen present as an excellent electron acceptor, electron transfer from dendron to core was observed. In the porphyrin-centered dendrimers, the benefit to having a complete shell was once again demonstrated as previously mentioned in Section 1.4.1.1. When a complete shell of benzyl ether dendrons surrounded the porphyrin core as in Figure 1.18, the energy transfer yield increased to 80%. With one to three dendrons present, energy transfer was only 10% to 32%. The dramatic increase was attributed to efficient energy migration throughout the dendron shell, analogous to the natural photosynthetic system.

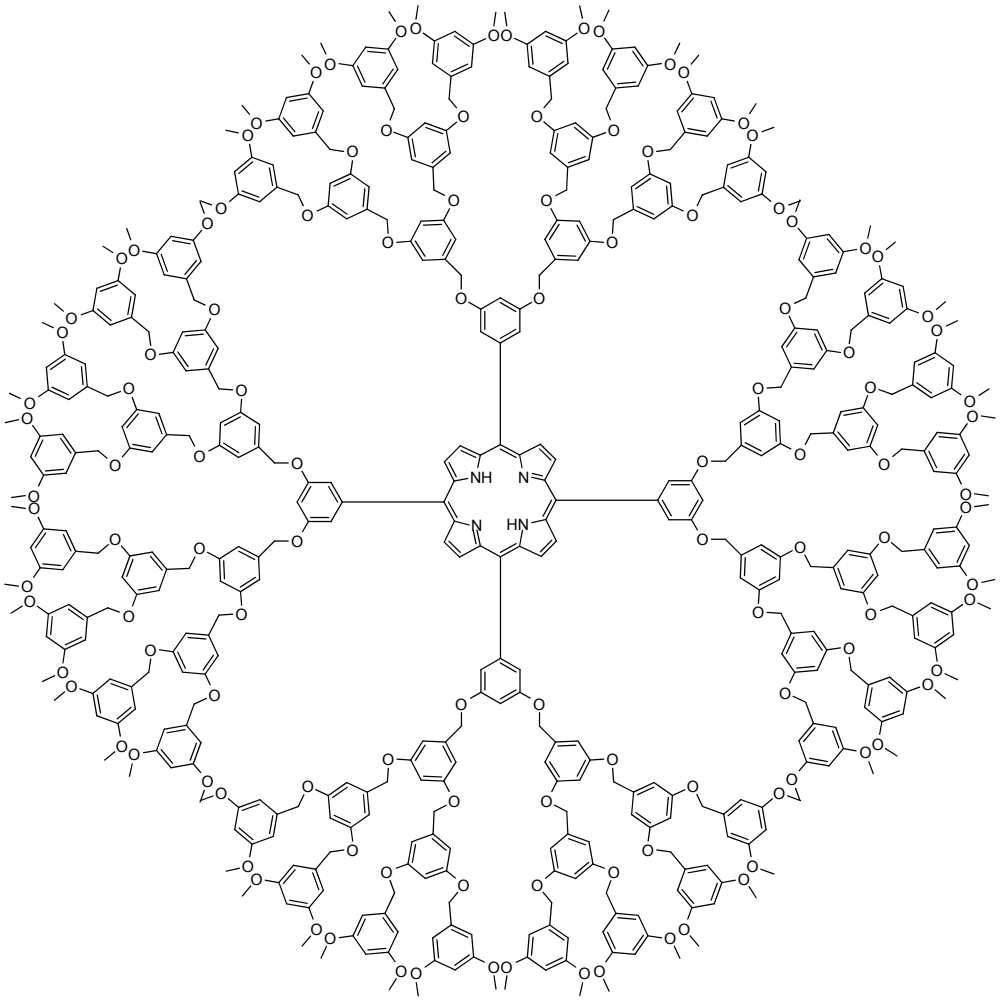


Figure 1.18. Light harvesting dendrimer in which energy absorbed by the benzyl ether dendrons is transferred to the porphyrin core.

1.4.2.2 Transfer to a metallic core

Energy transfer from dendron branches to a metallic core was reported by Kawa and Fréchet. They modified benzyl ether dendrons with carboxylate cores. The dendrons were then used as ligands with three lanthanide metal ions, Er^{3+}, Tb^{3+}, and Eu^{3+}. The dendrons were expected to act as a shell to isolate the metal ions and reduce self-quenching. However, enhancement of the

lanthanide luminescence was unexpectedly observed due to the antenna effect of the dendrons transferring energy which they absorbed to the metallic core as well.[80]

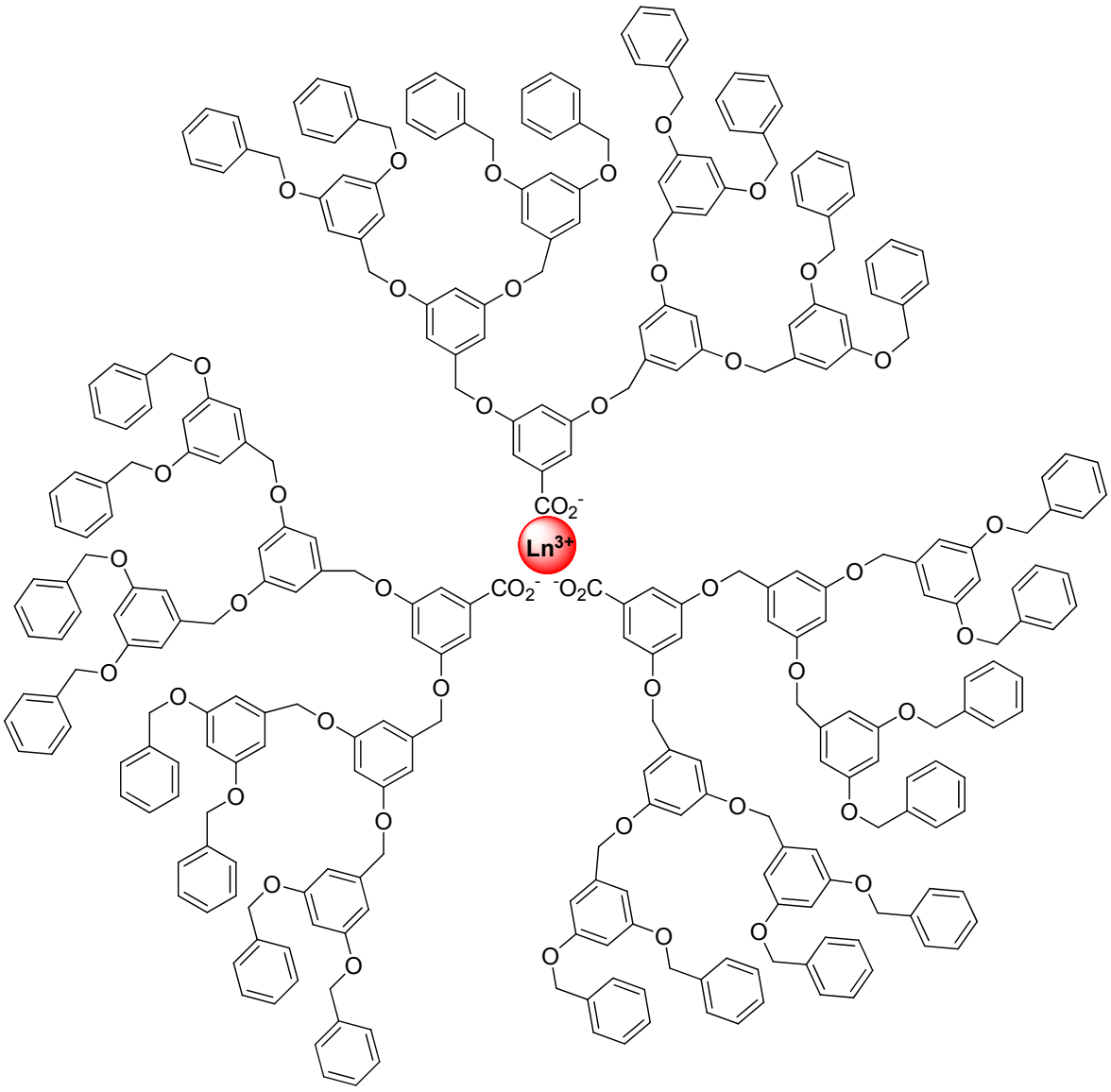


Figure 1.19. Benzyl ether dendrons modified to form dendrimers with metallic cores. Ln = Er, Tb, or Eu.

1.5 CONJUGATED DENDRIMERS

Dendrimers with π-conjugated systems are relatively less studied than their non-conjugated counterparts such as PAMAM, PPI, the Fréchet benzyl ether system or polylysine. PAMAM in particular is the most common dendrimer found largely due to its early synthesis and commercial availability. Conjugated dendrimers more rigid, shape-persistent structure and electronic and photophysical properties have not gone unrealized though, several having already been mentioned in the previous section for their use in light-harvesting systems. Conjugated dendrimers have also been investigated for their use in organic light-emitting diodes,[81] organic solid state lasers,[82] and preparation of metal-based nanoparticles.[83]

Upon review of conjugated dendrimers in the literature an ambiguity in the term "conjugated" is apparent. The subset of π-conjugated dendrimers fall in two categories: dendrimers with π systems exhibiting cross-conjugation and dendrimers with π systems exhibiting and extended, linear conjugation. A cross-conjugated compound has been defined as "a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other."[84] At a basic level then, assuming a conjugated molecule is one with alternating single and double bonds, in a cross-conjugated molecule two π systems will be conjugated with the third, but themselves will be separated by two single bonds.

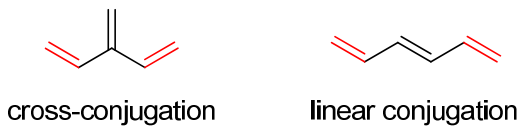


Figure 1.20. Cross versus linear conjugation in reference to the red π systems in each.

An alternative and still convenient way of describing cross versus linearly conjugated π-systems is to assign the atoms to sets according to alternant/nonalternant classification.[85, 86] The classification is useful for the prediction of reactivity and other properties of conjugated molecules. This system may be applied to any conjugated system by assigning each carbon with a p orbital to one of two sets: starred or unstarred. From the arbitrary starting point, the starring of atoms should alternate between the two sets. In the case of a ring of an odd number of atoms, it will be impossible to avoid to neighboring atoms being assigned to the same set and so these compounds are classified as nonalternant. If it is possible to star atoms on alternating π-centers and have no stars adjacent, then a conjugated system is present and the compound is said to be alternant.

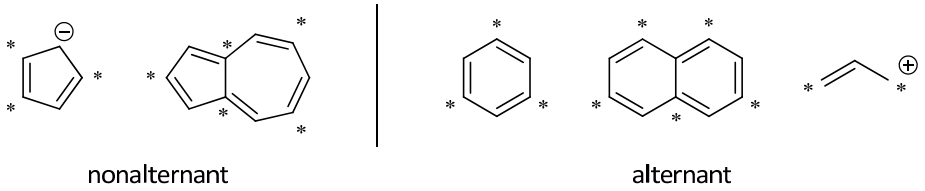


Figure 1.21. Examples of nonalternant and alternant conjugated π systems.

The difference between cross- and linearly conjugated systems when marked in this fashion is shown in Figure 1.22. Once the atoms have been starred and assigned to sets, they can be sorted into two categories based on the coupling between two ends of their structures: alike and disjoint. This is an important distinction when these compounds will be used as bridges between donors and acceptors for example. Cross-conjugated systems exhibit alike coupling. The atoms to which the donor and acceptor would be attached, drawn here as the left and right

ends of the structures belong to the same sets (starred or unstarred). Linearly conjugated systems demonstrate disjoint coupling; the atoms at either end belong to different sets.

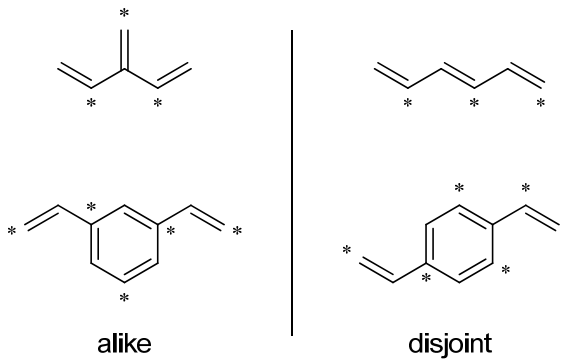


Figure 1.22. Assignment of atoms to starred and unstarred sets for a pair of cross-conjgated and a pair of linearly conjugated compounds allows their differention into which exhibit alike or disjoint coupling.

Whether there is alike or disjoint coupling is important to predicting the electronic coupling of the two compounds attached to the conjugated bridge. Cross-conjugated compounds, those with alike coupling, are known to have very low electronic coupling while linearly conjugated systems, those that are disjoint, have high coupling.[87, 88] The coupling through a bridge is related to the molecular orbital coefficients.[87] In a cross-conjugated system, it can be anticipated the there will be zeros in the electronic coupling that are not present in a linearly conjugated system. Figure 1.23 shows the HOMO and LUMO for divinyl substituted benzenes similar to those shown in Figure 1.22. In the *meta*-substituted example, in both the HOMO and LUMO, there is within the ring, between the branches at which there is zero contribution from the atomic orbitals.

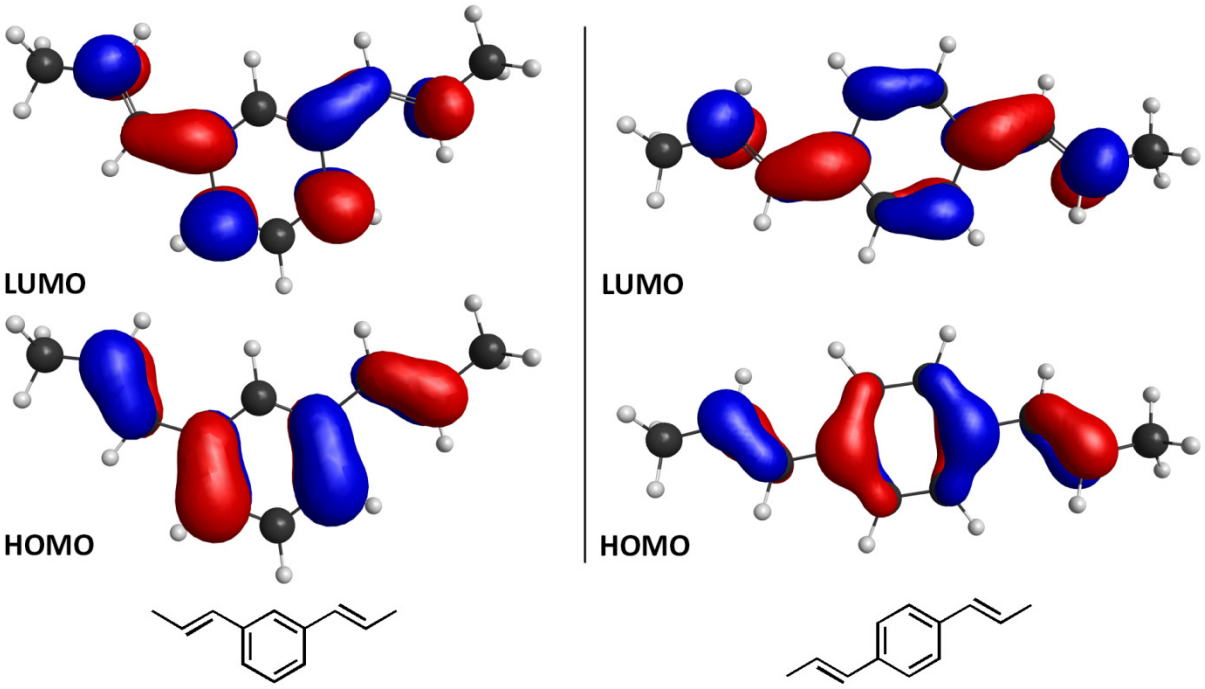


Figure 1.23. HOMO and LUMO molecular orbitals of *meta*- and *para*- substituted π systems.[89, 90]

Cross-conjugated and linearly conjugated systems also differ in their UV-vis spectra. In the case of dendrimers with extended, linearly conjugated systems, the spectrum shows a red-shift with increasing generation as the effective length of the π-conjugation increases. Many instances of conjugated dendrimers fall into the cross-conjugated subset, perhaps because the symmetry of the 1,3,5-substituted benzene ring has an aesthetic appeal that fits well with general aesthetics of dendrimer synthesis. To expand on previous examples, if branching is via benzene subunits, this will occur whenever two branches are related in a *meta* fashion. Dendrimers with linearly π-conjugated systems will have alternating single and double bonds on a path from periphery to core which occurs when the branching is done in a *para* fashion. Dendrimers with

ortho branching would also technically possess linear π conjugation, though the twists in these systems are a hindrance to extending conjugation.

1.5.1 Cross-Conjugated Dendrimers

1.5.1.1 Dendrimers based on the 1,3,5 phenylene vinylene motif

Dendrimers with the 1,3,5 phenylene vinylene motif are among the most widely studied of dendrimers with conjugated systems.[46, 81, 91-109] A common focus of research with these dendrimers is their luminescence properties, often with the possible application in organic light-emitting diodes as a stated goal. Other work has investigated ferrocene-cored dendrimers for data storage[95] or dendrons with a fullerene core for light-harvesting.[46]

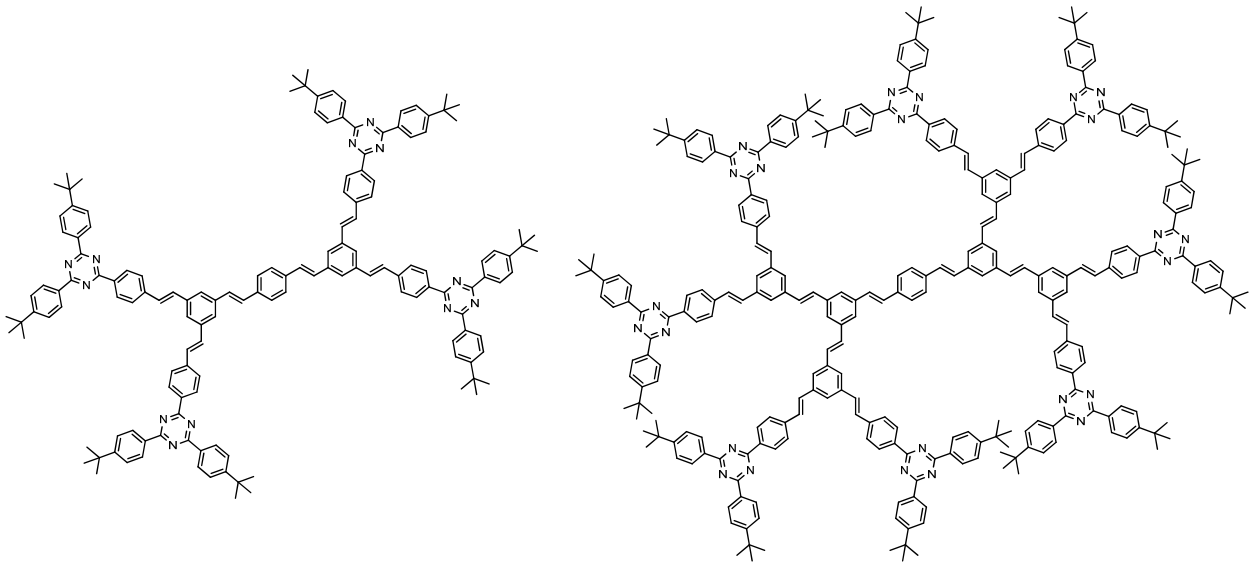


Figure 1.24. Generations 1 and 2 1,3,5-substituted phenylene vinylene dendrimers with cross-conjugated π-systems.[96]

1.5.1.2 Dendrimers based on the 1,3,5-phenylene ethynylene motif

Closely related are the 1,3,5-phenylene ethynylene based dendrimers.[70, 110-113] While no extended π system is present in these to broaden their absorption characteristics, these were studied for their use in light harvesting. Devadoss *et al*. demonstrated the use of an energy gradient with 1,3,5-phenylene ethynylene based dendrimers previously discussed (Section 1.3.2.1) by introducing an additional acetylene spacer near the core, thus lowering the energy of that chromophore. The cross-conjugation of the branches allows them to function independently. In this way, a gradient from periphery to core of longer and longer branches is used for energy transfer.[70] Due to their rigid structure, these dendrons were attached to BINOL cores and used as asymmetric catalysts. The dendron-modified BINOL showed much higher catalytic activities versus unmodified BINOL.[110]

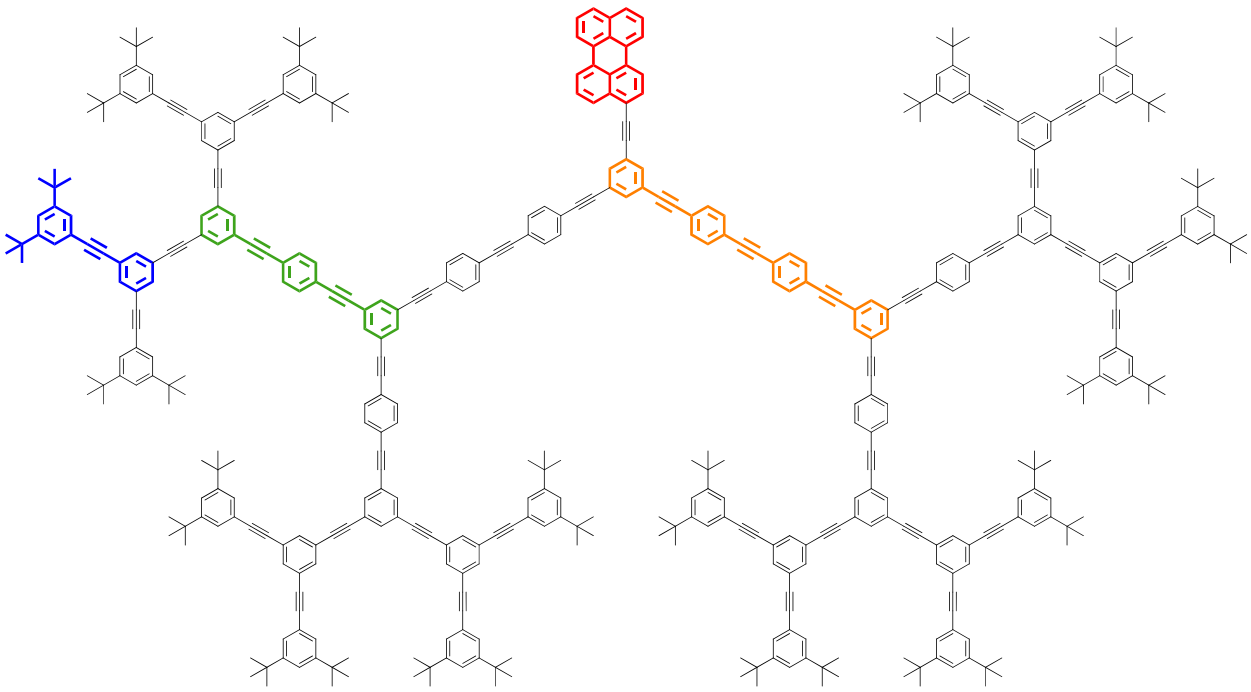


Figure 1.25. 1,3,5-substituted phenylene ethynylene dendron with added spacers. Chromophores of increasing linear conjugation length (blue, green, orange) are highlighted along with perylene (red) which compose the energy gradient.[70]

1.5.1.3 Dendrimers based on truxene

Another example of cross-conjugated dendrimers are the truxene-based materials prepared by Pei *et al*.[76, 114-121] These drew attention first for their potential as light-harvesting dendrimers[76, 115-117] and then later as blue organic light-emitting diodes.[118-121] The truxene structure leads branches of the dendrimer to be cross-conjugated. Extended π-conjugation was ruled out as the λ_{max} of the dendrimers from G0 through G2 remained around 350 nm meaning the effective conjugation length was not increased.[117, 118] Instead, in order to alter the optical

properties and to install a gradient in these compounds short π-conjugated spacers were added such as thienylethynylene,[76, 115, 116, 119] or phenylene vinylene.[120, 121]

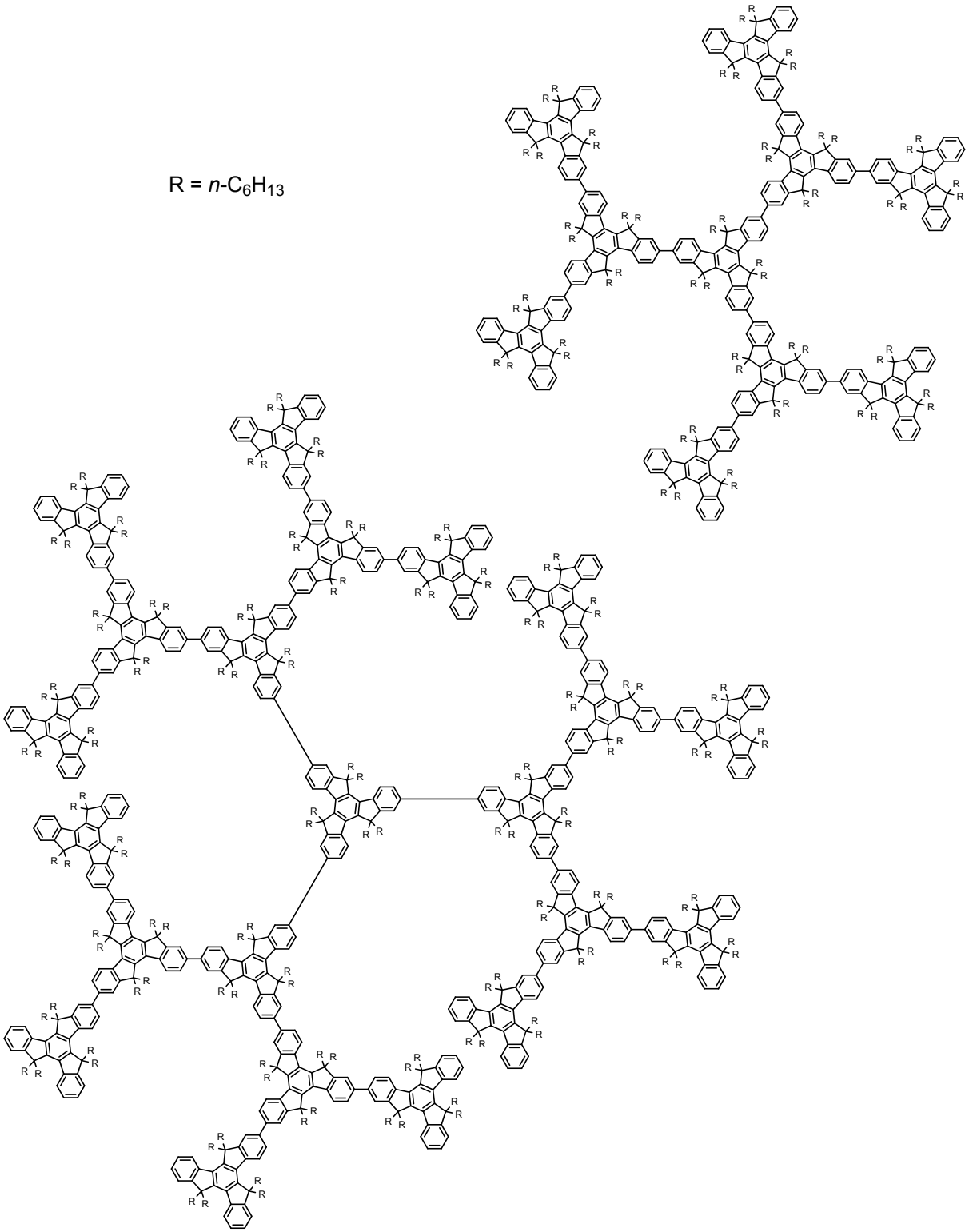


Figure 1.26. Truxene dendrimers with cross-conjugated branches.[117]

1.5.1.4 Dendrimers based on pentaphenylbenzene

Polyphenylene dendrimers have been reported as well.[62-64, 67, 68] They have been used as an invisible scaffold for a series of dyes in order to study energy transfer between the dyes. The dendrimers are poor chromophores and show none of the characteristics of other conjugated dendrimers. This is due to their sterically-strained, twisted pentaphenylbenzene units which do not show any evidence of extended conjugation.

1.5.1.5 Other Dendrimers with cross-conjugation

Other examples of cross-conjugated dendrimers are few. Interesting though is their application. Rather than use as organic light-emitting diodes or light harvesters, carbazole based dendrimers have been used to prepare xerogel films for the detection of explosives.[122] Triphenylamine based polymers were studied for the relationship between increasing generation and enhanced two-photon absorption.[123]

1.5.2 Dendrimers Combining Cross-Conjugation & Extended, Linear π-Conjugation

1.5.2.1 Dendrimers based on 1,3,4-phenylene ethynylene motif

The 1,3,4-phenylene ethynylene motif is an interesting one as it provides a combination of types of conjugation in each dendron.[72-74, 124-126] Through the *para*-related branches there is linear π-conjugation while between *meta*-related linkages there is only cross-conjugation. This leads to a broad absorption from the dendrimer backbone stretching from 240 nm to 430 nm due to the differing effective conjugation lengths of the various branches. These structures also possess a natural energy gradient from periphery to core as the conjugation lengths increase. These two properties have made these compounds targets for light-harvesting applications. It is

anticipated that these dendrimers will be better energy transfer funnels than their *meta*-linked analogs due to the fact the *para* substitution provides a through-bond charge-transfer mechanism.[124]

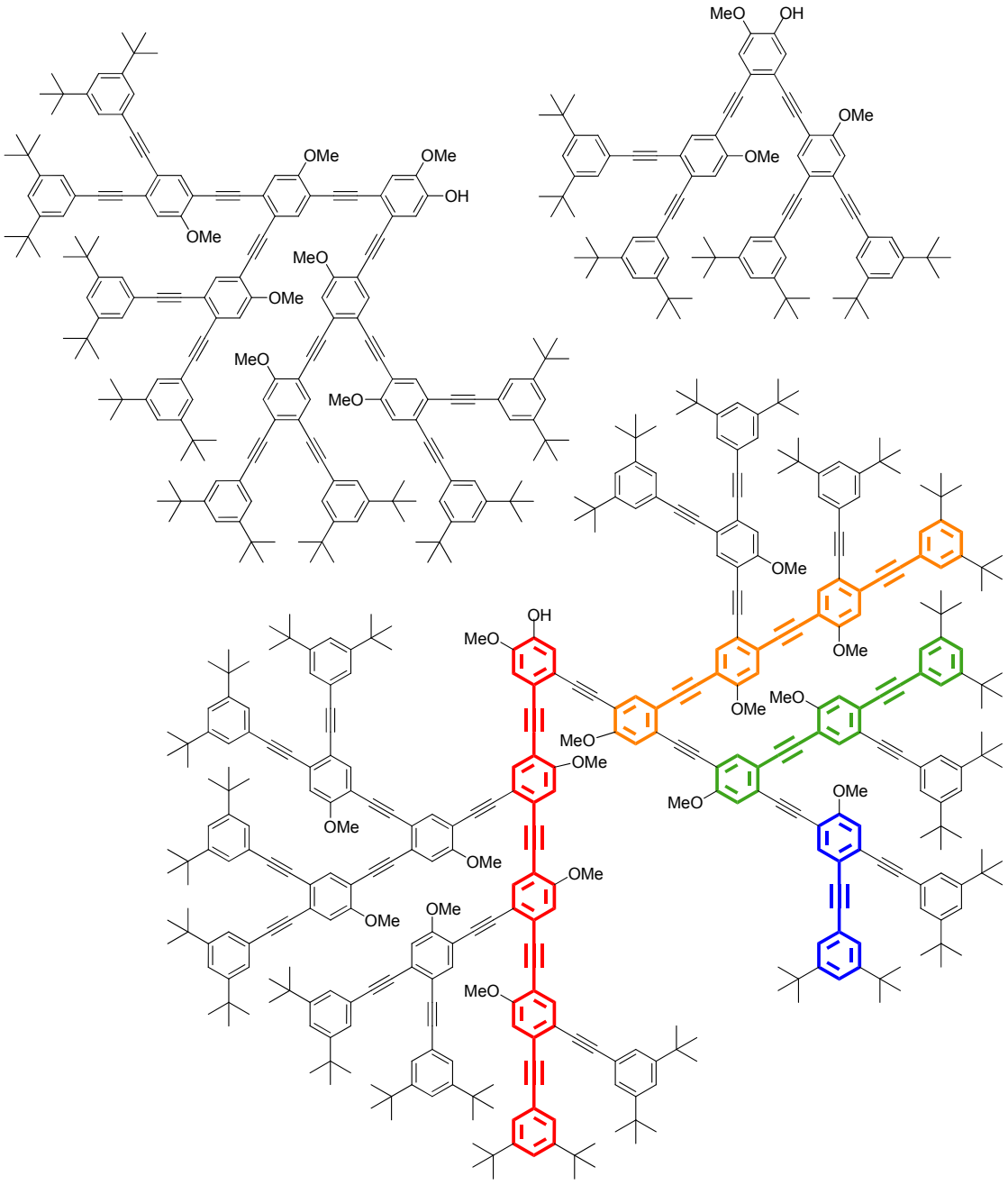


Figure 1.27. 1,3,4-substituted phenylene ethynylene dendron with a combination of cross-conjugated and linearly conjugated branches. Cross-conjugation leads to branches of different effective conjugation noted by the colored segments.[124]

1.5.2.2 Dendrimers based on thiophene

Thiophene based dendrimers also contain both cross-conjugated branches as well as branches with extended π-conjugation. Following the first synthesis,[127] various other thiophene-based dendrimers were reported and their properties were further elucidated.[128-131] It was found that as early as the second generation, gains in optical absorption from the extended π-conjugation were decreasing. This was attributed to steric forces causing the dendrons to twist out of plane, limiting the effective conjugation length.[129] As with other conjugated dendrimers, thiophene systems have primarily been investigated for their optical properties, especially their application in light harvesting.[131-136]

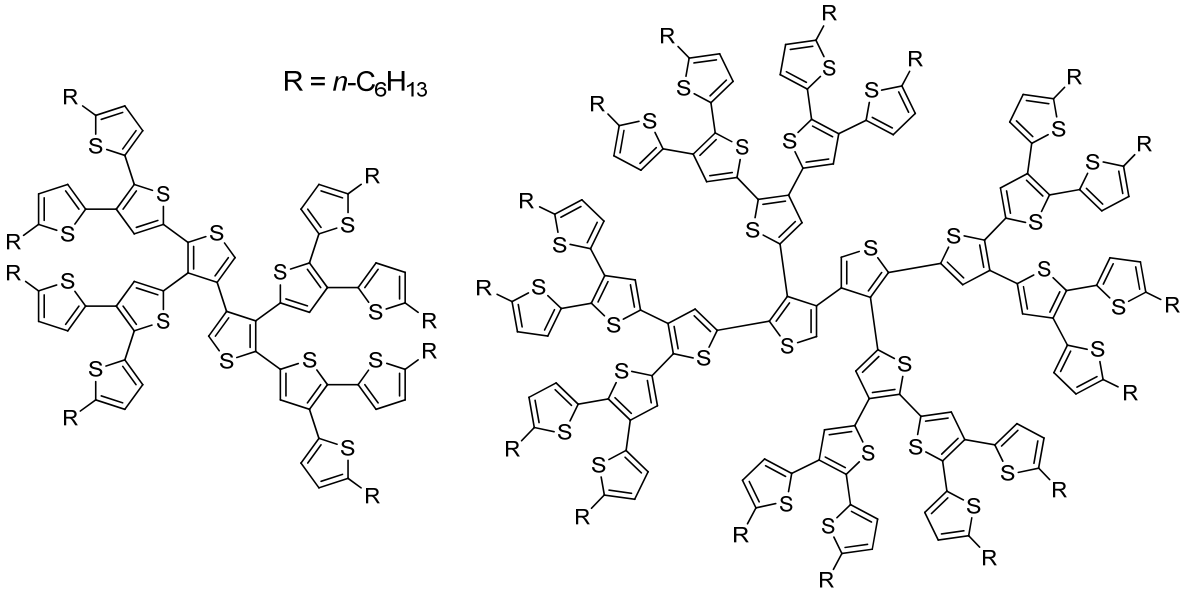


Figure 1.28. Generations 2 and 3 thiophene dendrimers which contain both cross-conjugated and linearly conjugated branches.[117]

1.5.3 Dendrimers with Extended, Linear π-Conjugation

1.5.3.1 Dendrimers based on diphenylazomethine

Examples of dendrimers in which all the branches are in extended π-conjugation are scarce. Those based on diphenylazomethine by Yamamoto et al. are one example of this structural feature.[83, 137-142] Since the first report on their preparation,[138] a new synthetic route was found that reduced the necessary starting material to only 1/176 of the amount required by the original method.[140] With greater access to these materials, their metal coordinating function, including an unusual step-wise, generation by generation coordinating property has been investigated.[137, 141, 142] They have also been used as a template to prepare quantum size titanium oxide[83] and in preparation of dye-sensitized solar cells as a charge separator to inhibit back electron transfer.[139]

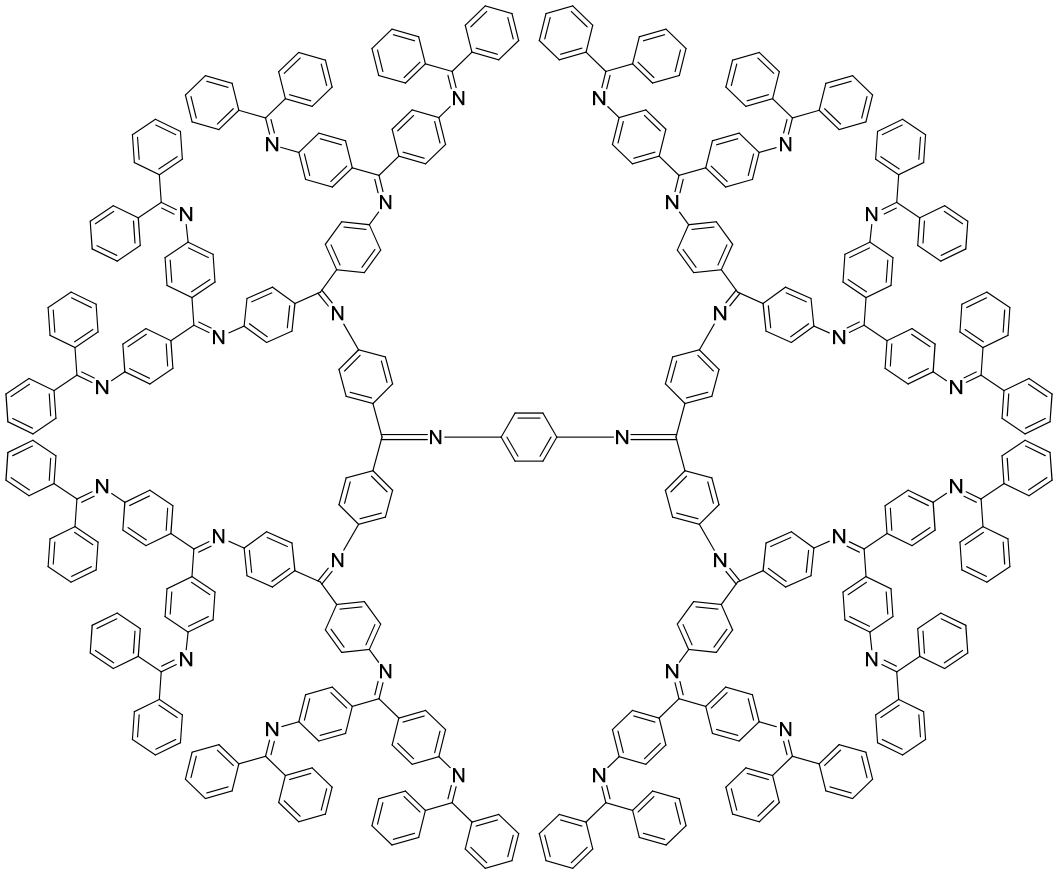
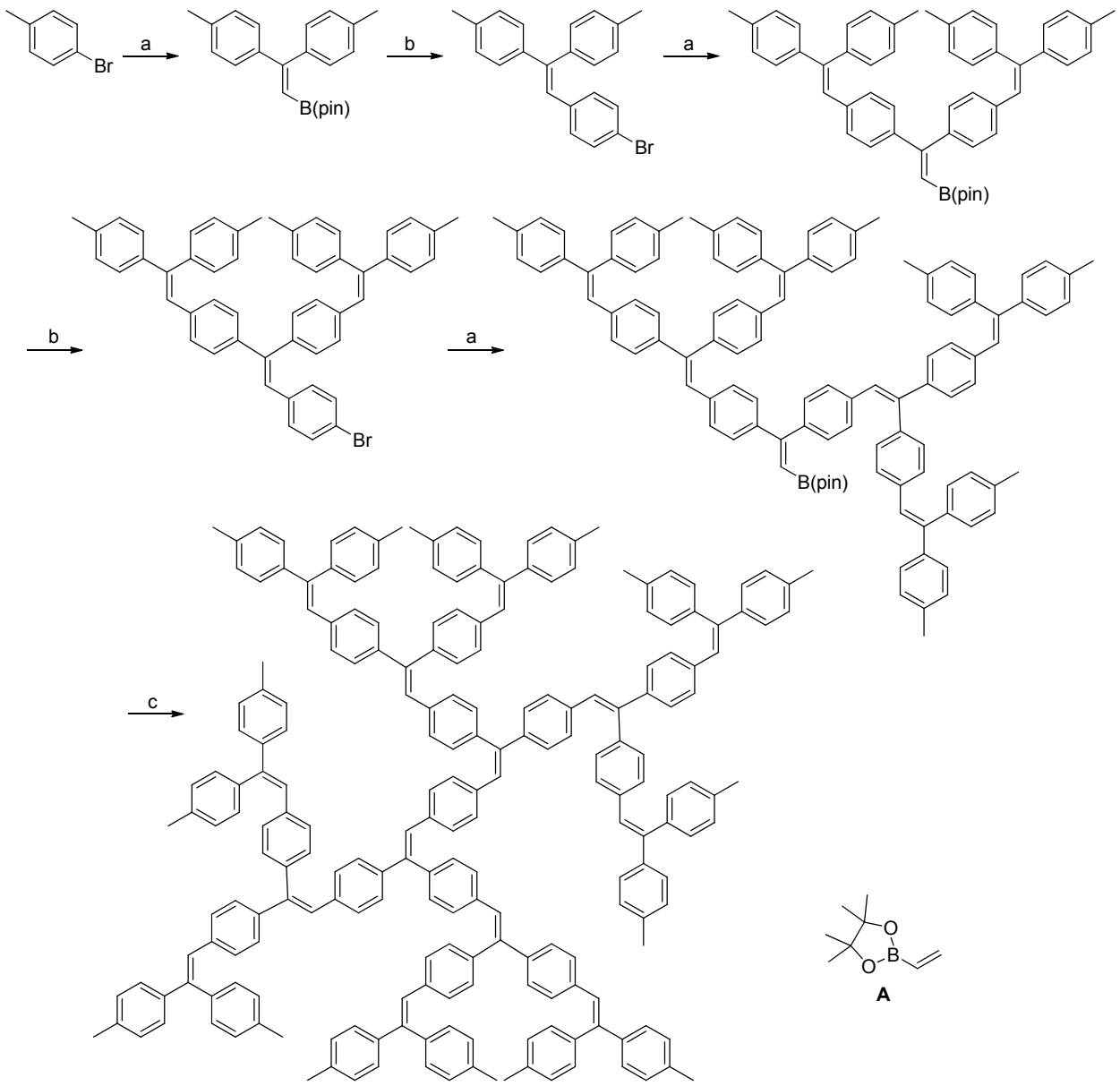


Figure 1.29. Fourth-generation diphenylazomethine dendrimer.[138]

1.5.3.2 Dendrimers based on a 1,4-phenylene vinylene motif

Unlike the phenylene vinylene dendrimers mentioned previously, if branching occurs at the vinyl moiety as opposed to the phenyl moiety, the resulting structure can have extended π-conjugation through all its branches. Itami et al. were the first group to have reported the synthesis of these triarylethylene based dendrimers.[143] They prepared a series of dendrimers up to generation three as a demonstration of chemistry they had developed for the preparation of triarylethenes using a double Heck-type arylation followed by a single Suzuki coupling. In 2012,

a second report[144] of the preparation of *p*-phenylene vinylene dendrons by Yamamoto and coworkers based on our synthesis[145] was made.



Scheme 1.1. Synthesis of 3rd generation 1,4-substituted phenylene vinylene dendrimer. [143]

Reagents and Conditions: (a) **A**, $Pd[P(t\text{-}Bu)_3]_2$, iPr_2NH, toluene, 80 °C; (b) 1-bromo-4-iodobenzene, $Pd(PPh_3)_4$, aq. Cs_2CO_3, toluene, 90 °C; (c) 1,4-diiodobenzene, $Pd[P(t\text{-}Bu)_3]_2$, NaOH, H_2O, toluene, 90 °C.

1.6 CHARGE TRANSFER IN DENDRIMERS

1,4-Substituted phenylene vinylene dendrimers are of special interest beyond their limited examples in the literature. Nearly all reports in the literature of light-harvesting by dendrimers have been instances of excitation energy transfer either from chromophores arranged around the periphery or from the dendrons themselves to a core acceptor chromophore. This mimics the first stages of the natural photosynthetic unit where the light is initially absorbed by the LH1 and LH2 antennae. From those subunits, the energy is transferred rapidly and efficiently to the reaction center. In the reaction center, that energy is changed to chemical energy via a charge separated state.

Reports of charge transfer in dendrimers are much more uncommon. Phenylene vinylene dendrons with a 1,4-substitution pattern could be especially well-suited for electron transfer. These are essentially highly branched oligo(phenylene vinylene) (OPV). OPVs are excellent candidates for use as molecular wires. A molecular wire is molecule that bridges a donor and an acceptor through which an charge is transferred. Usually, as distance increases, the rate of charge transfer decreases. However, with molecular wires this distance dependence is very weak resulting in the ability to transfer charge over long distances.

The ability of *p*-phenylene vinylene oligomers to behave as molecular wires was demonstrated in the system show in Figure 1.30. Tetracene donors were physically linked with pyromellitimide acceptors by oligophenylene vinylene bridges. Over short distances there was a strong distance dependence for the systems with only a benzene or stilbene bridge. At longer lengths though, the rate of electron transfer increased dramatically as seen in Figure 1.31. This was attributed to a switch in the mechanism of transfer to one that utilized the bridge as a molecular wire.

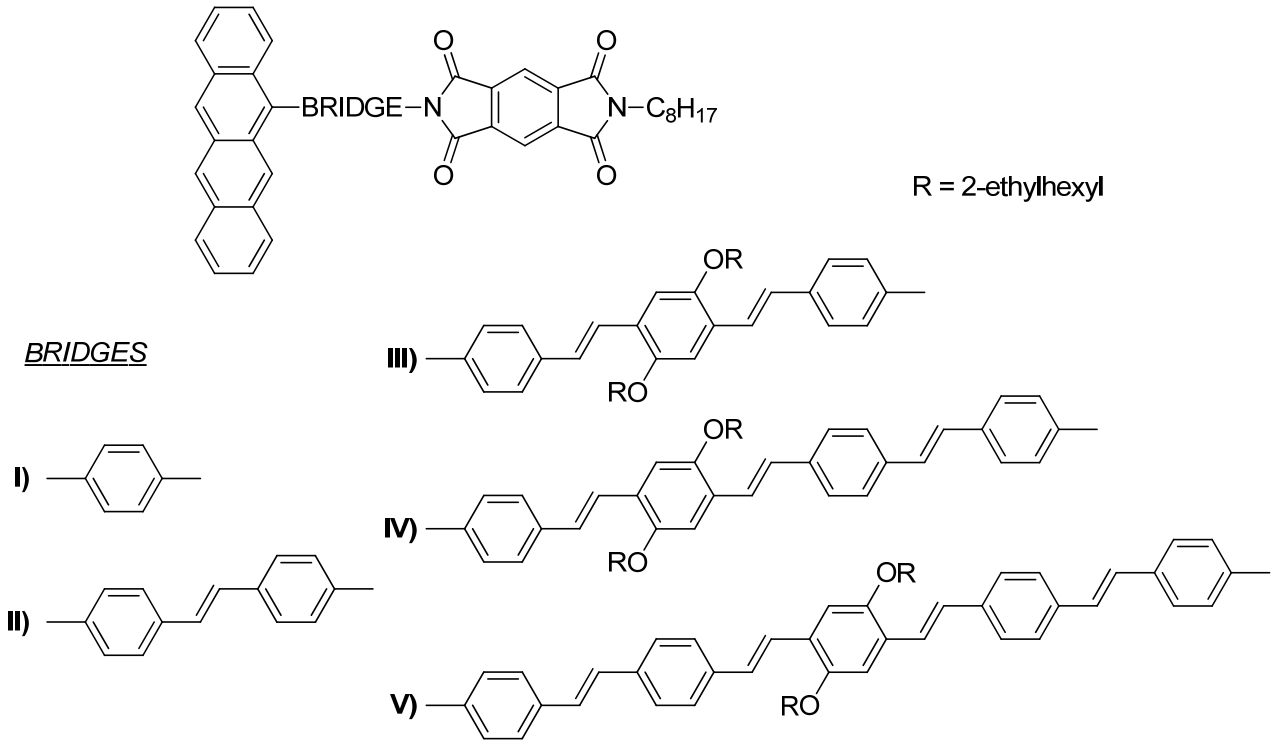


Figure 1.30. Oligo(phenylene vinylene) molecular wire compounds

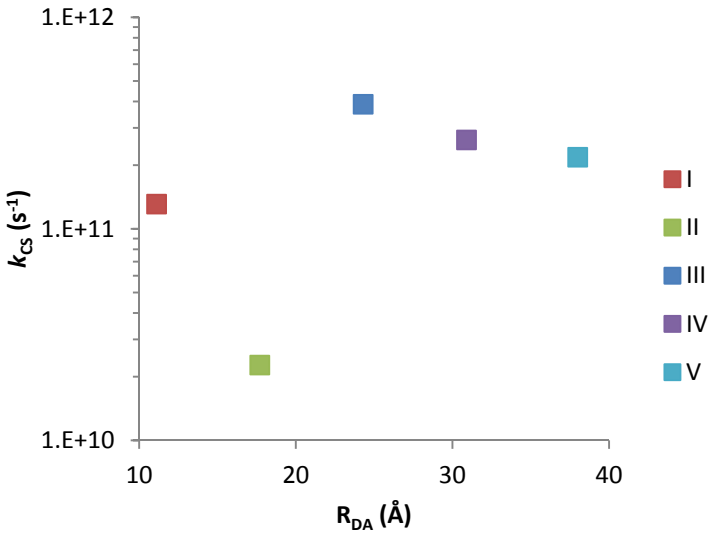


Figure 1.31. Distance dependence of charge separation rate constants for OPVs.[146]

Moreover, the phenylene vinylene system has been shown to be a better molecular wire than other systems, including others with extended π-conjugation. Compared to an alkane bridge, the OPV system has a conductance measured to be three orders of magnitude greater. This would be expected, as the π system is invoked in explanation of the decrease in distance dependence of those systems. However, the OPV system has also been found to be approximately ten times better than phenylene ethynylene systems.[147]

A *p*-phenylene vinylene dendron could behave similarly acting as a bridge between multiple peripheral donor chromophores and an acceptor at the focus. If donors were able to efficiently and rapidly transfer electrons to the core, a benefit to electron transfer could be realized similar to the gains seen with energy capture and transfer, the antenna effect, observed in dendritic light harvesting systems already discussed. If a large absorption cross-section from multiple chromophores arranged on the periphery of a dendron were to be combined with rapid and efficient electron transfer via a phenylene vinylene molecular wire dendron to a reactive core, the system would be an excellent candidate for solar energy harvesting and conversion.

2.0 SYNTHESIS OF *p*-PHENYLENE VINYLENE DENDRONS

When work on these dendrimers began, there were no previous reports of their synthesis. Since then, two other instances of their preparation have appeared, one using the method reported here. Based on examples of *meta*-substituted phenylene vinylene dendron synthesis at the time work began, this method utilizes a Horner-Wadsworth-Emmons condensation in the key bond forming step leading to higher generation dendrons. A convergent strategy was chosen that would build these dendrons from the outer shell inwards. This is advantageous compared to a divergent approach as there are fewer active reaction sites during each reaction leading to greater reaction completion. The products would also be more easily purified as the properties of those molecules that did not undergo complete reaction would be easily differentiated from those molecules which did completely react.

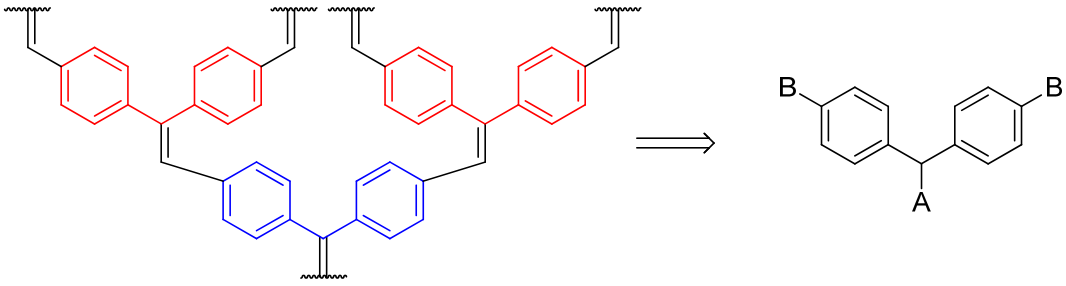


Figure 2.1 Retrosynthetic analysis of *p*-phenylene vinylene dendron structure.

One analysis of the structure of *p*-phenylene vinylene dendrons yields a benzhydryl core as the key repeating unit shown in Figure 2.1. Key to the controlled, generation-by-generation

synthesis of dendrimers is the masking of reactive sites or the choice of functional groups that can easily be converted into reactive moieties. In choosing the Horner-Wadsworth-Emmons condensation as the key bond-forming step, groups **A** and **B** would be either a carbonyl (ketone if **A** or aldehyde if **B**) or a phosphonate as shown in Figure 2.2.

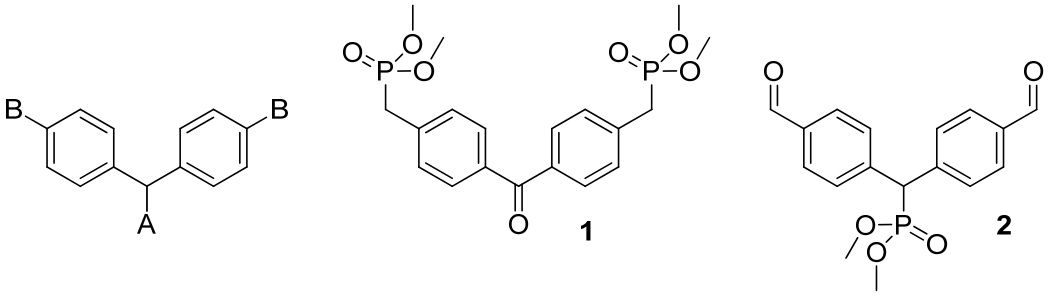


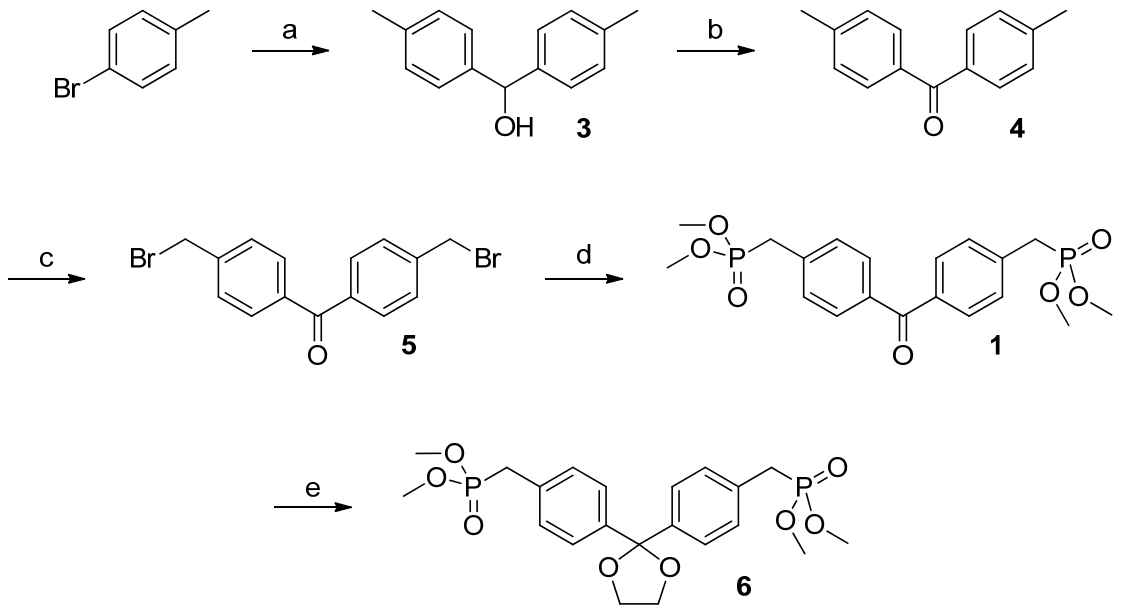
Figure 2.2 Two possible monomers for a Horner-Wadsworth-Emmons based synthesis of *p*-phenylene vinylene dendrons.

2.1 SYNTHESIS UTILIZING A BENZOPHENONE-DERIVED MONOMER

Because a convergent strategy was desired, and the ketone functionality could be easily recovered from an acetal, the monomer **1** was chosen with the ketone at the core and phosphonate diesters at the *para* position of each phenyl unit. As the dendrons were synthesized, there would be only one deprotection reaction at one site per molecule intermediate to dendron growth.

Synthesis of benzophenone **1** began with 4-bromotoluene as shown in Scheme 2.1. After lithiation and addition of two equivalents to ethyl formate, the benzhydrol **3** was formed in excellent yield. Compound **3** could be recrystallized from hexanes, however the reaction often

was so clean, that the crude product could be used in the next step with no problems. Oxidation of the alcohol using Anelli's protocol[148, 149] led to facile conversion to the benzophenone **4**. As hoped, this product was easily recrystallized from ethanol. Wohl-Ziegler radical bromination in dichloroethane led to the dibromobenzophenone **5** in very good yield. Treatment with trimethylphosphite gave the phosphonate diester **1**. Recrystallization of this product was possible using ethyl acetate. Lastly, protection of the ketone as the ethylene acetal **6** provided for the protection of the carbonyl as would be required during dendron synthesis. The acetal was an ideal protecting group in this instance as it could be removed with simple, mild, high-yielding conditions in preparation for further dendron growth or other functionalization for incorporation into light harvesting systems.

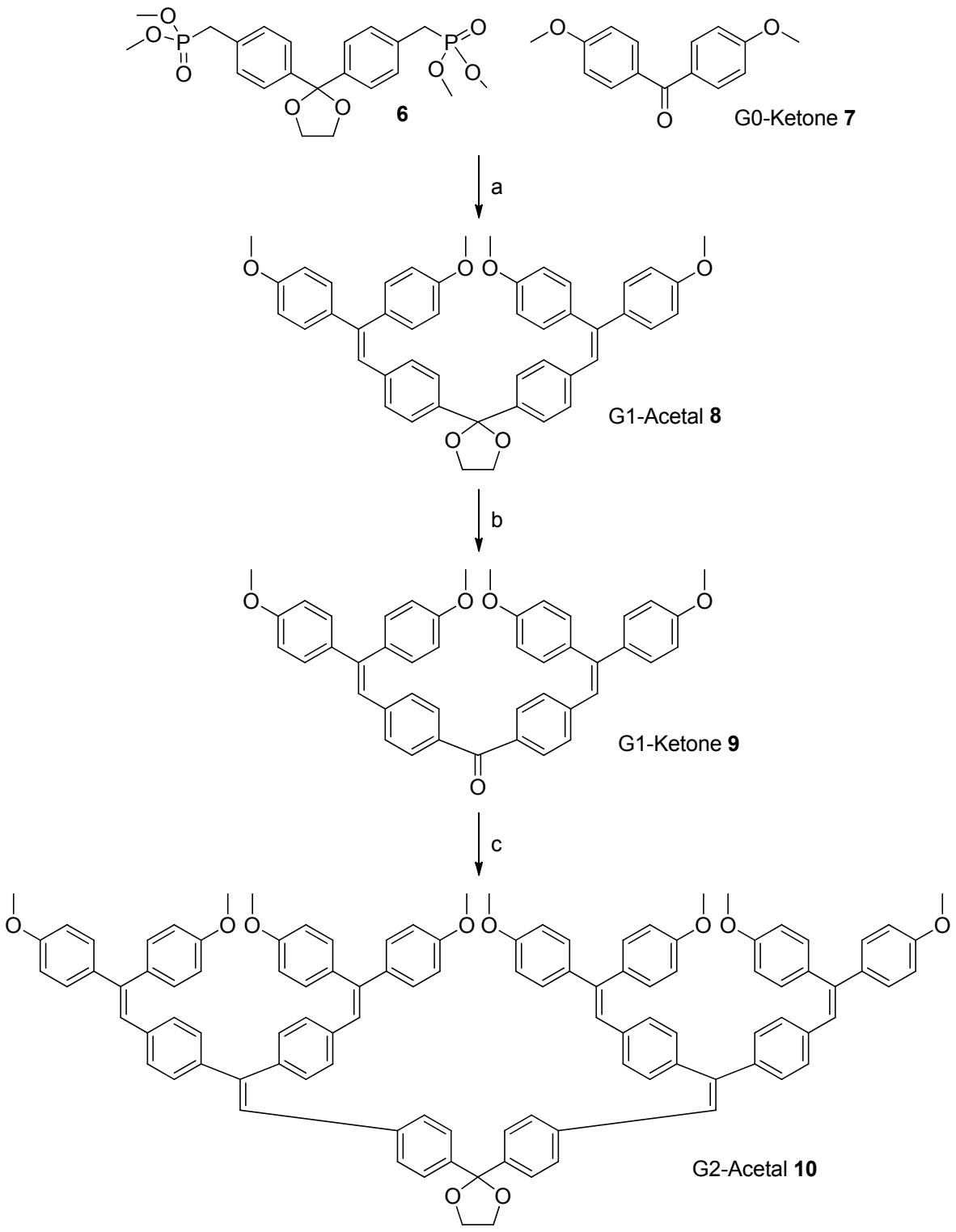


Scheme 2.1. Synthesis of bisphosphonate monomer for *p*-phenylene vinylene dendron synthesis.

Reagents and Conditions: (a) i) *n*-BuLi, hexanes, THF -78°C, ii) ethyl formate, THF, warm to RT; (b) TEMPO, NaOCl, KBr, CH_2Cl_2, 0°C, 92% (over two steps); (c) *N*-bromosuccinimide, benzoyl peroxide, 1,2-dichloroethane, reflux; (d) $P(OMe)_3$, PhMe, reflux, 60% (over 2 steps); (e) ethylene glycol, TsOH, PhMe, reflux, 85%.

With the monomer **6** in hand, synthesis of the dendrons was undertaken as shown in Scheme 2.2. As the phosphonates could not easily be masked or converted into another inert group, methyl ethers were chosen as a peripheral group. It was anticipated these could be easily removed for later functionalization of the periphery. Also, 4,4'-dimethoxybenzophenone (G0-Ketone **7**) was readily available and inexpensive. Therefore, 4,4'-dimethoxybenzophenone was added to the anion of phosphonate **6** prepared with sodium hydride. Upon workup, the benzophenone was recovered and no product was obtained. Unexpectedly, the benzylphosphonate anion formed by sodium hydride is unstable when heated.[150, 151] In light of this finding a switch to potassium *tert*-butoxide was made. Addition of this base to a 0 °C

solution of G0-Ketone **7** and phosphonate **6** yielded the first generation dendrimer **8**, G1-Acetal, as a light yellow solid. Deprotection with *p*-toluenesulfonic acid gave G1-Ketone 9 as an intensely-colored, bright yellow solid in near quantitative yield. Condensation of G1-Ketone **9** with **6** yielded the second generation dendron G2-Acetal **10** with eight peripheral methyl ethers and the acetal at the focal point.



Scheme 2.2. Synthesis of first two generations of a *p*-phenylene vinylene dendron.

Reagents and Conditions: (a) KO*t*Bu, DMF, 0°C, 69%; (b) TsOH, H_2O, acetone, 100%; (c) **6**, KO*t*Bu, DMF, 0°C, 26%.

During purification by chromatography, the G1-Ketone **9** formed clear, yellow needles in the most concentrated fractions. These needles were suitable for X-ray crystallography, and the structure was determined as shown in Figure 2.3. The structure reveals that the rings are not coplanar. The deviations are only enough to relieve steric interactions while maintaining the conjugation along the branches. Measurements of the dihedral angles between the π systems of a branch are given in Table 2.1. Molecular modeling of the crystal structure to find the minimized equilibrium geometry was carried out. Using semi-empirical methods, the structure became quite distorted from the crystallographic structure. Using the B3LYP density functional theory method with STO-3G basis set yielded a minimized structure that was a very close match to the crystallographic structure. This indicates that the dendron does not take on an otherwise unusual structure when in the crystal lattice.

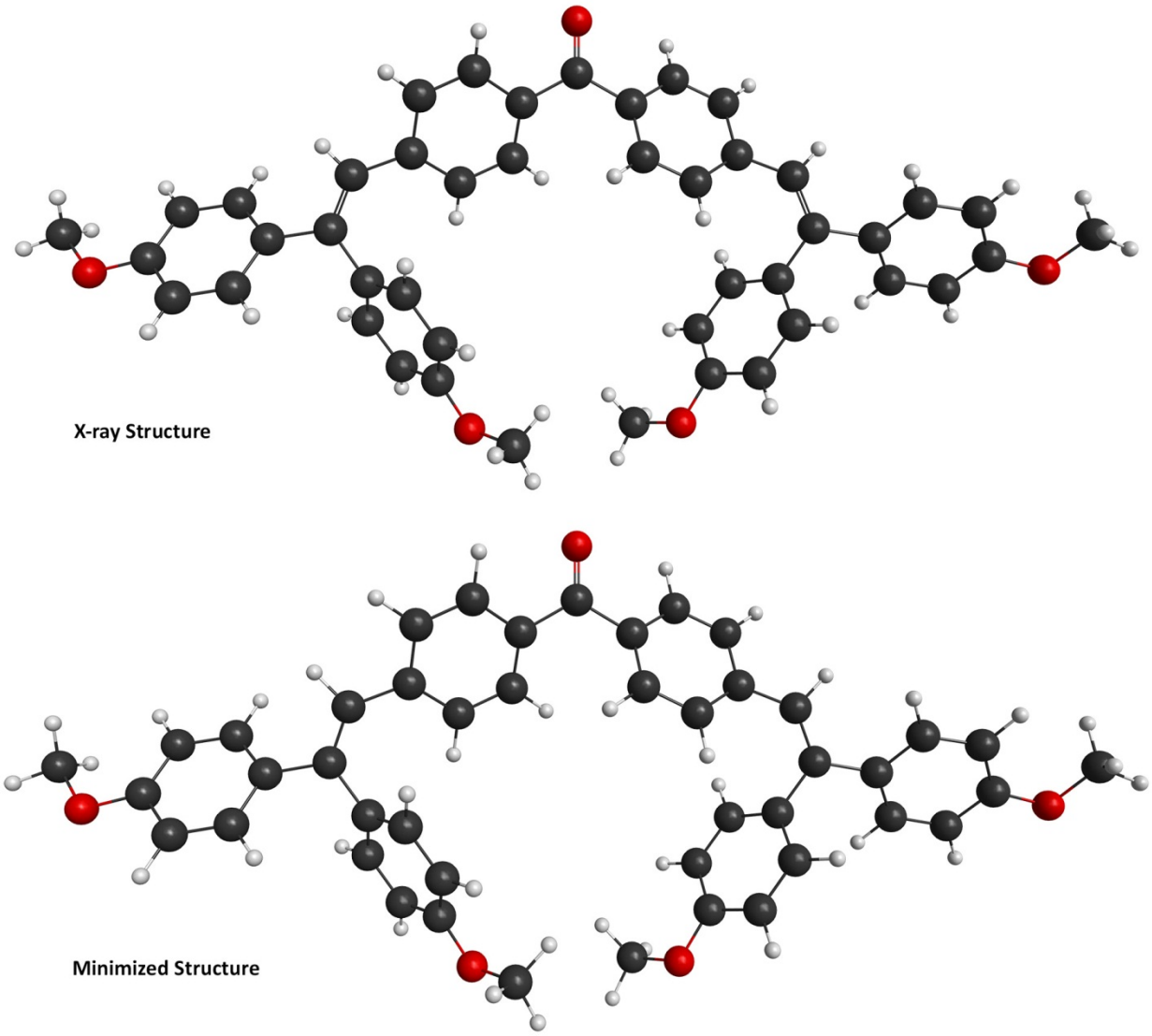
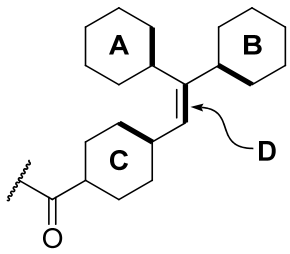


Figure 2.3. X-ray crystal structure of G1-Ketone **9** and DFT B3LYP[152] minimized structure.

Table 2.1. Dihedral angles between π-systems of G1-Ketone **9**.

π systems	crystallographic dihedral angle	DFT-minimized dihedral angle
A—D	51.15°	51.92°
B—D	36.41°	36.61°
C—D	24.14°	24.81°



In addition to crystallographic data for G1-Ketone **9**, the structure of the dendrons was confirmed by ^{1}H and ^{13}C NMR and high-resolution mass spectrometry. For the first generation dendrons, especially useful was the $-OCH_3$ from the periphery. This signal split into two singlets, each integrating to six hydrogen. Also informative was the appearance of the vinylic protons present in these structures. The region immediately downfield of the vinyl protons became more complicated due to the number of similar, but not identical, signals for the aryl protons. Here, the use of a higher field 500 MHz instrument was sufficient to deconvolute the region and identify the expected doublets for each set of aryl hydrogens. In analysis of the ketone, a switch to deuterated acetone was also helpful as the vinylic protons have the same chemical shift as some of the aryl protons when the spectrum is recorded in deuterated dichloromethane. In each case, the ^{13}C NMR showed the predicted chemical shifts and number of peaks for each compounds. The symmetry of the compounds and of portions of branches combined with the non-planarity leads to several pairs of nuclei that are nearly, but not in exactly identical chemical environments. Therefore, several pairs of peaks are apparent with very little difference in their chemical shifts, similar to the $-OCH_3$ signals observed in the ^{1}H NMR spectra. See Appendix A for copies of the spectra of these compounds.

G2-Acetal **10** was analyzed in the same fashion as the first generation dendrons. In this case, the aryl region now had too many overlapping signals making deconvolution impossible. Despite this, the integration of the various peaks in the aryl/vinyl region did match the expected value. More clear was the doubling again in the number of peaks assigned to the $-OCH_3$ groups. In the ^{1}H NMR spectrum for G2-Acetal **10**, there were now four, closely spaced singlets that each integrated to six for these methyl ether protons. The carbon nuclei of these ethers only give two distinguishable signals however. Similar pairing of related carbon were seen in the second

generation dendron as was described in the first generation dendrons. Lastly, high-resolution mass spectrometry was also found to support the synthesis of the second generation acetal.

The preparation of G2-Acetal **10** was accompanied by a precipitous drop in yield. Whereas the Horner-Wadsworth-Emmons condensation to give G1-Acetal **8** proceeded with an acceptable, if unspectactular, 69% yield, the preparation of G2-Acetal **10** only gave 26% yield. This decrease is similar to that observed in the other reported syntheses of *p*-phenylene vinylene dendrons where a drop from 76% to 33% between generation one and generation two was reported.[143] Convergent syntheses are known to be best for preparation of lower generation dendrimers, usually up to three or four generations. The difficulty in preparing higher generation dendrimers is generally attributed to steric crowding as the increasingly large dendrons need coupled with the relatively small inner branching unit. In the case of phenylene vinylene dendrons, this is likely an especially important factor, due to the rigidity of the phenylene vinylene backbone imposing even greater restrictions.

To investigate the presence of extended π-conjugation in the prepared dendrons, UV-visible absorption spectra were recorded and presented in Figure 2.4, Figure 2.5, and Table 2.2. A comparison of dendrons with a ketone at the apex, G0-Ketone **7** and G1-Ketone **9** supports the presence of the extended π-conjugation. A 78 nm shift of λ_{max} from 292 nm to 370 nm was found. A comparison of the compounds bearing an acetal at the apex showed a similar bathochromic shift. In a comparison of G1-Acetal **8** and G2-Acetal **10**, a shift of λ_{max} from 328 nm to 350 nm is recorded.

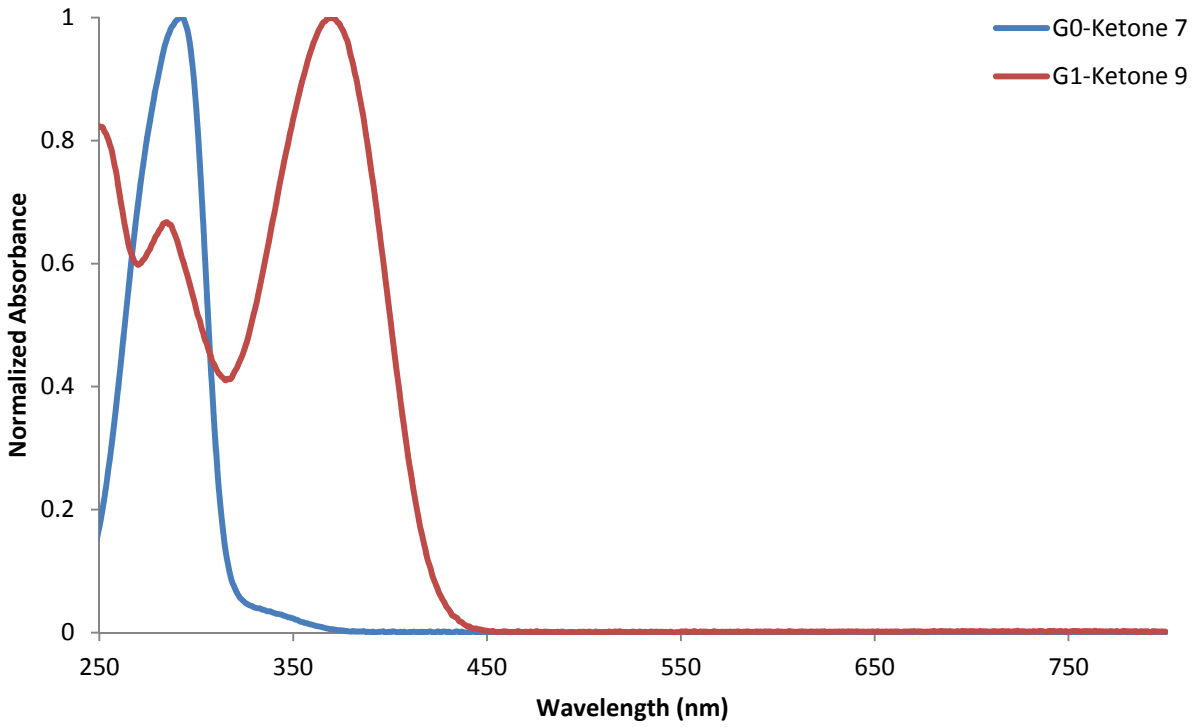


Figure 2.4. Normalized UV-vis absorption spectra of G0- & G1-Ketone.

Experimental Conditions: Collected in dichloromethane. [G0-Ketone **7**] = 1.4 x 10^{-5} M; [G1-Ketone **9**] = 5.3 x 10^{-6} M. Spectra normalized to λ_{max} of each compound.

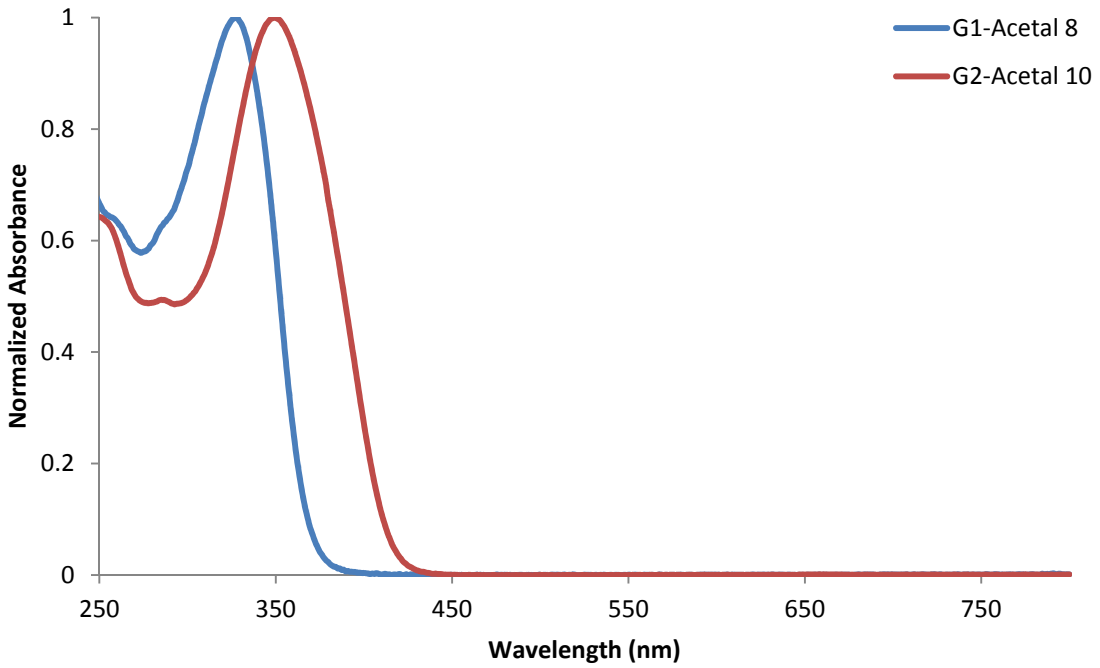


Figure 2.5. Normalized UV-vis absorption spectra of G1- & G2-Acetal.

Experimental Conditions: Collected in dichloromethane. [G1-Acetal **8**] = 5.2 x 10^{-6} M; [G1-Acetal **10**] = 5.5 x 10^{-6} M. Spectra normalized to λ_{max} of each compound.

Table 2.2. UV-Vis absorption data for dendrons.

Compound	λ_{max} (nm)	ϵ ($L \cdot mol^{-1} \cdot cm^{-1}$)
G0-Ketone **7**	292	25,717
G1-Ketone **9**	250	34,536
	285	28,002
	370	41,949
G0-OTBS **16**	264	61,057
G1-OTBS **19**	236	30,482
	319	37,131
G1-Acetal **8**	236	43,129
	328	52,859
G2-Acetal **10**	285	56,294
	350	114,016

All spectra collected in dichloromethane.

2.2 SYNTHESIS UTILIZING A BENZHYDRYL-DERIVED MONOMER

An alternate synthesis of *p*-phenylene vinylene dendrons also showed the same extension of the π system. The alternate synthesis was based on monomer **2** with reversal of the phosphonate and carbonyl functional groups versus the arrangement in **1**. Moreover the alternate synthesis was to have aldehydes at the periphery for later functionalization which could be masked as acetals during construction of the dendrons. This was of consequence because all the initial reactants for the dendron synthesis were derived from a common precursor **12**.

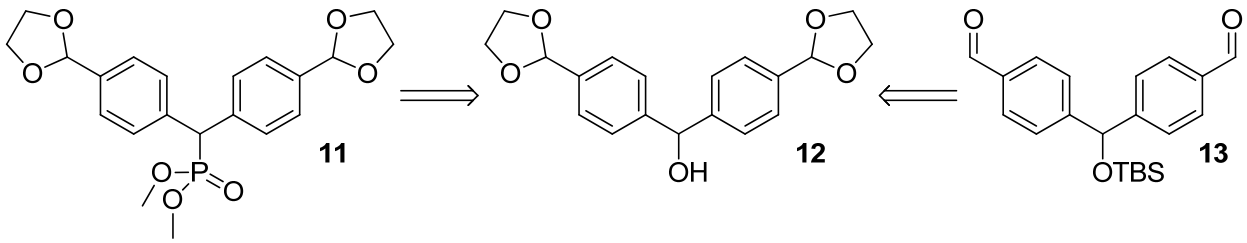
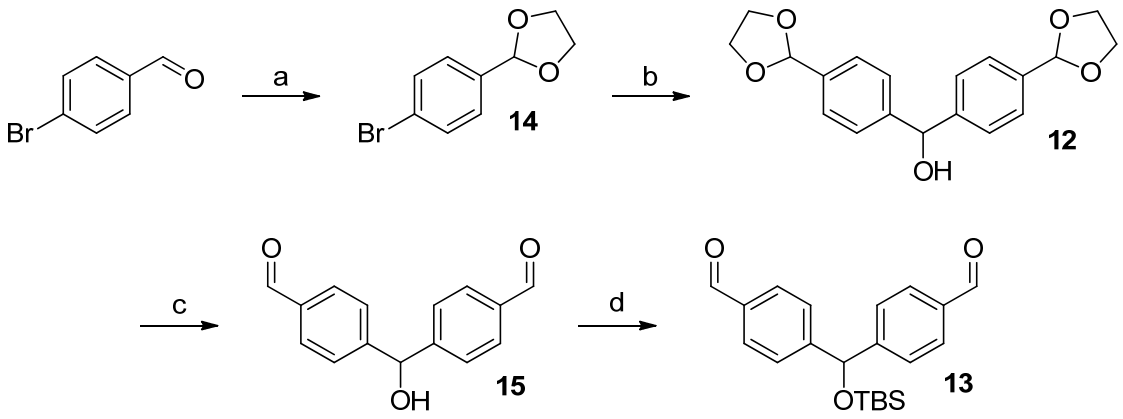


Figure 2.6. Building blocks for alternate synthesis of dendrons are derived from a common precursor.

The monomer was to be synthesized as shown in Scheme 2.3. 4-bromobenzaldehyde was protected as the ethylene acetal **14**. Then, in a manner similar to the synthesis of the previous monomer, the acetal was lithiated and underwent condensation with ethyl formate to give benzhydrol **12**. Hydrolysis of the acetals followed by protection of the alcohol gave the TBS ether **13**.

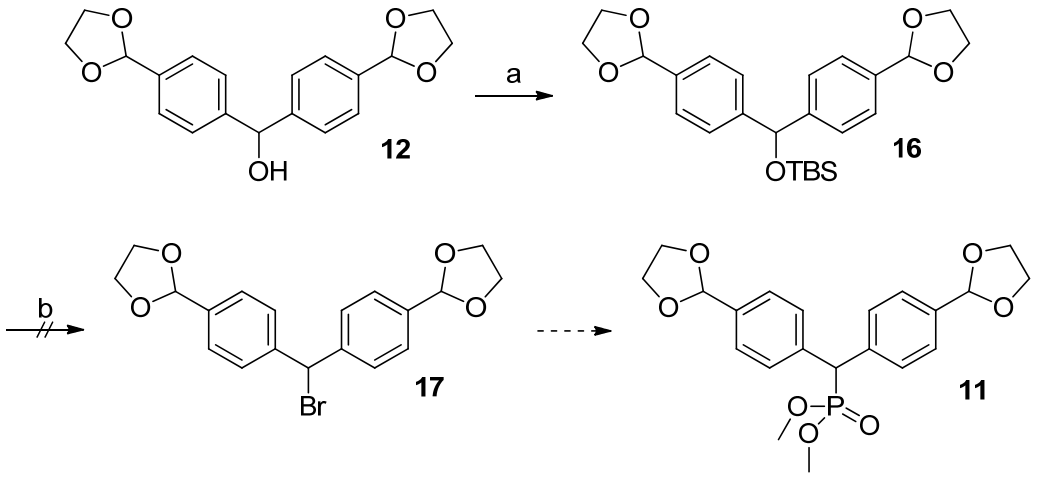


Scheme 2.3. Preparation of monomer **13** for alternate dendron synthesis.

Reagents and Conditions: (a) ethylene glycol, TsOH, PhMe, reflux, 94%; (b) i) *n*-BuLi, hexanes, THF, -78°C, ii) ethyl formate, THF, warm to RT, 89%; (c) TsOH, H_2O, acetone; (d) TBSCl, imid, DMF, 63% (2 steps).

Benzhydrol **12** was also silylated in order to prepare the benzhydryl phosphonate **11** necessary for reaction with the dialdehyde **13**. TBS ether **16** was treated with PPh_3Br_2 intending to isolate the corresponding benzhydryl bromide.[153] However, these conditions led to an inseparable mixture from which deprotected aldehydes were recovered as well as the benzhydrols resulting from desilylation. Suspecting small amounts of acid present from reaction of trace amounts of water with the PPh_3Br_2 to be the culprit of these unwanted transformations, the reagent was instead prepared *in situ* using carbon tetrabromide and triphenylphosphine, thereby avoiding the introduction of any HBr that had formed in the commercially available reagent. This variation led to the same mixture of products however. Further investigation revealed that the conditions used for the desired direct conversion of TBS ethers to bromides also effected the undesired deprotection of the acetals[154] and so other conditions were sought that had

been originally dismissed due to the prospective toll additional steps would take as each successive generation was prepared.

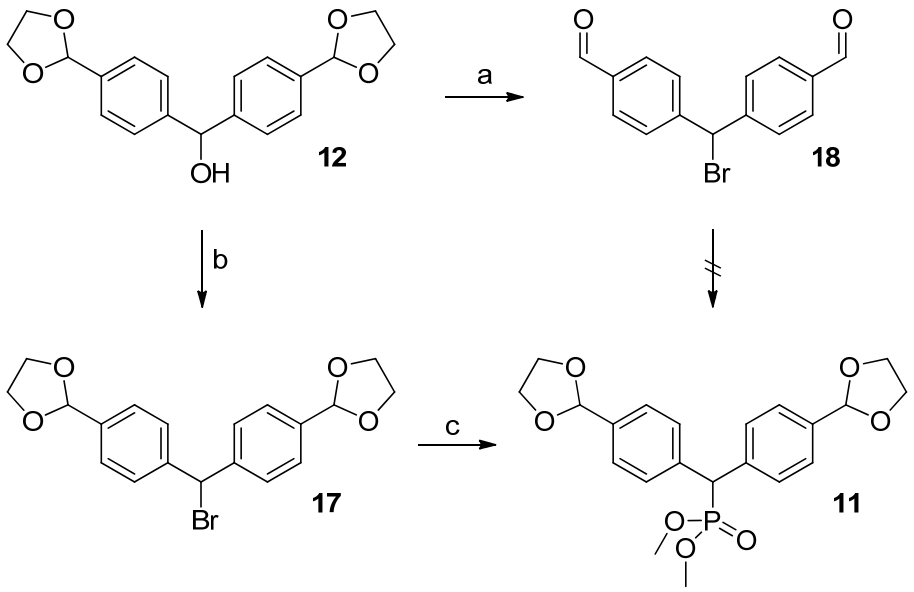


Scheme 2.4. Attempted preparation of phosphonate **11** to be used in alternate dendron synthesis.

Reagents and Conditions: (a) TBSCl, imid, DMF, 59%; (b) PPh_3Br_2 or CBr_4/PPh_3, CH_2Cl_2.

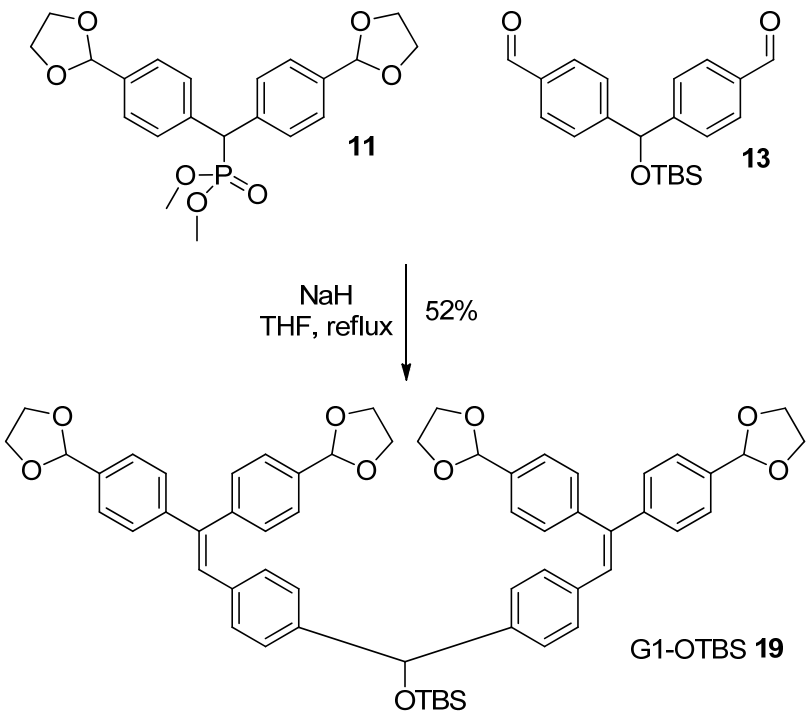
Conversions which utilized an alcohol at the core were explored as desilylation was expected to be a high-yielding, clean reaction which would have a minimal impact on higher generations. Therefore, the synthesis of the phosphonate sans acetals was attempted as shown in Scheme 2.5 with the intent that aldehydes could be reprotected at a later stage also in good yield. The bromodialdehyde **18** was prepared by refluxing **12** with aqueous HBr. Unfortunately, attempts for conversion of **18** to the benzhydryl phosphonate **11** were futile. Finally, a route with yet more steps necessary between the potential synthesis of each generation of phenylene vinylene dendron was attempted. Instead of direct conversion of the benzhydrol **12** to the bromide, an intermediate mesylate would be prepared. This route was beneficial in that the aldehydes would not require reprotection after synthesis of the phosphonate, but otherwise held little benefit. Using this route, benzhydryl bromide **17** was isolated and converted to the desired phosphonate **11**. This route however suffered from low yields, making it impractical to use in

preparation of higher generations given then increasing value. Additionally, it was found that the bromides were extremely prone to hydrolysis due to the highly stable benzhydryl cation. This factor was especially apparent as a varying amount of the inseparable benzhydryl chloride was isolated during the synthesis of **17** as a result of latent chloride ions remaining in solution from the preparation of the mesylate.



Scheme 2.5. Preparation of benzhydryl phosphonate **8** for dendron synthesis.
Reagents and Conditions: (a) conc. HBr, CH_2Cl_2, reflux, 94%; (b) i) MsCl, NEt_3, THF, 0°C, ii) LiBr, warm to RT, 59%; (c) $P(OMe)_3$, reflux, 41%.

With a small quantity of benzhydryl phosphonate **11** that was prepared, the Horner-Wadsworth-Emmons condensation with dialdehyde **13** was carried out as shown in Scheme 2.6. In this manner the first generation *p*-phenylene vinylene dendron G1-OTBS **19** was prepared in 52% yield. Using this, the extended π conjugation in these dendrimers was again shown by the UV-visible absorption of the dendrons as shown in Figure 2.7. Compared to the similarly substituted G0-OTBS **16**, a red-shift in λ_{max} from 264 nm to 320 nm was observed.



Scheme 2.6. Synthesis of *p*-phenylene vinylene dendron **19** via alternate approach with reversed reactivity.

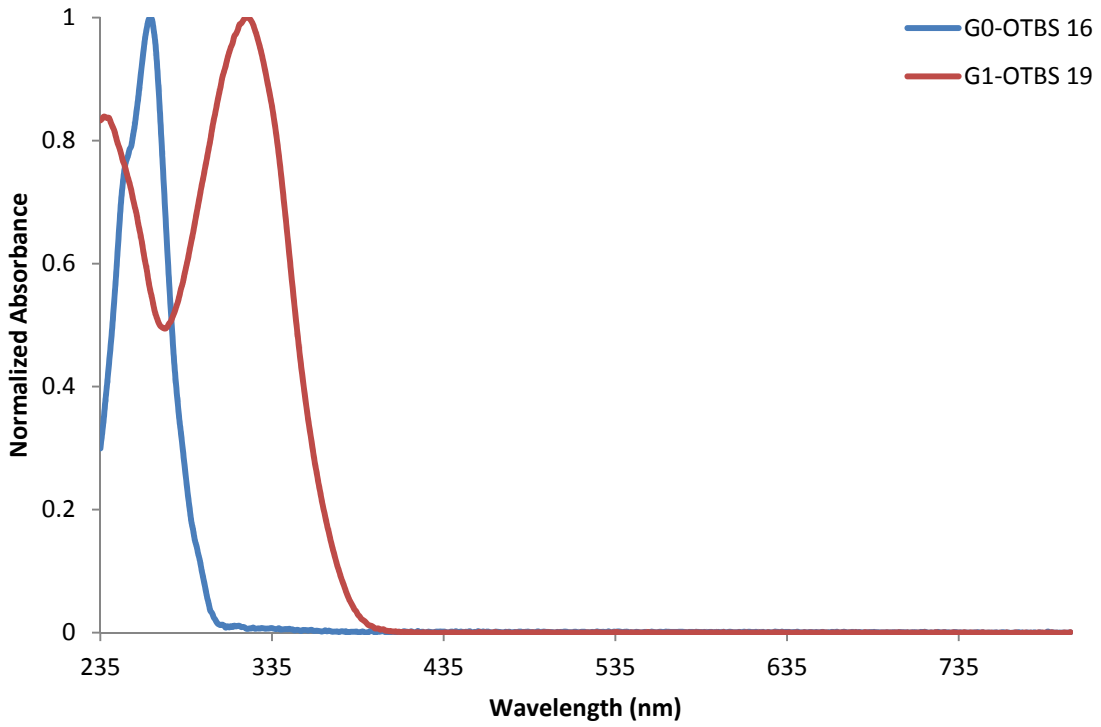
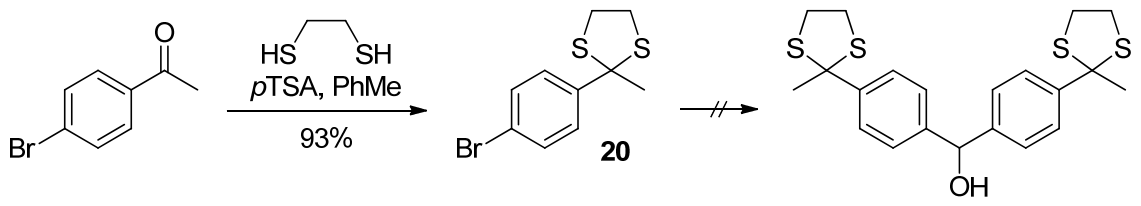


Figure 2.7. Normalized UV-vis absorption spectra of G0- & G1-OTBS.

Experimental Conditions: Collected in dichloromethane. [G0-OTBS **16**] = 5.6 x 10^{-6} M; [G1-OTBS **19**] = 5.3 x 10^{-6} M. Spectra normalized to λ_{max} of each compound.

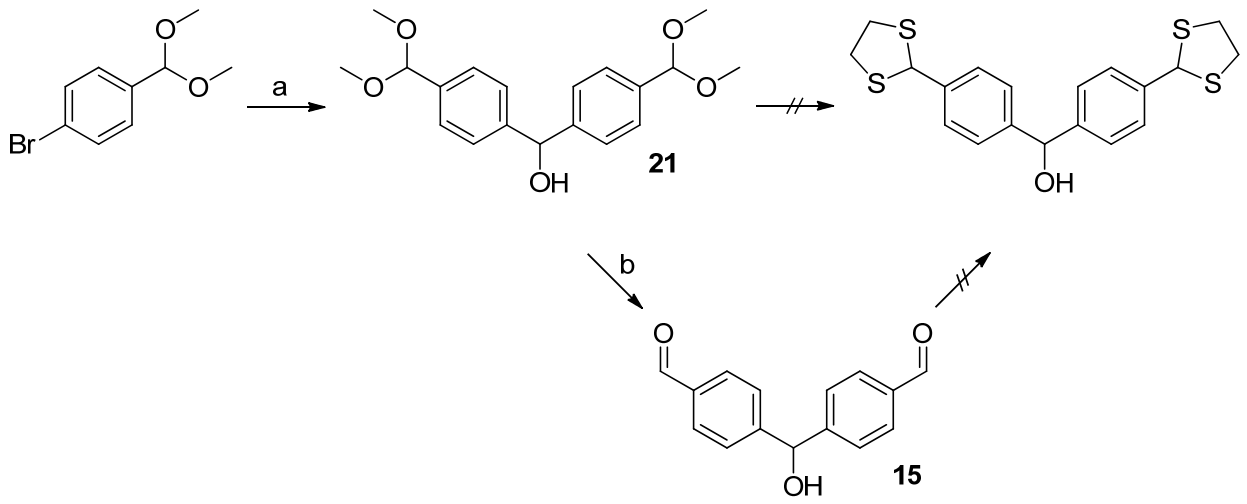
Characterization of G1-OTBS **19** dendron utilized the same techniques used in analysis of dendrons prepared via the benzophenone-derived monomer in Section 2.1. Similar to the –OCH_3 peaks which doubled in number with each generation of the previously described dendrons, the four benzyl protons at the periphery of **19** showed the same division into two close peaks. The vinylic protons were not separate from the aryl peaks. Instead, they centered within the farthest upfield of those aryl signals; the integration of six for the peaks centered at 7.00 ppm (versus four for the other aryl signals) was an indication of their presence in addition to the third peak tucked inside the double at the same chemical shift. The ^{13}C NMR spectrum and high-resolution mass spectrometry data matched expected values as well.

After the work up to this point, the acetals were clearly not robust enough to work in this synthetic approach. The number of steps needed to prepare the monomer compounds was prohibitive, all the more so when considering the dendrons would be undergoing the same transformations intermediate to successive generations. A carbonyl protecting group more stable to acidic conditions was necessary. Thioacetal analogs were considered for this reason. The acidity of the carbonyl hydrogen once protected as a thioacetal was problematic during construction of the monomer however. Therefore, acetophenone was considered in which the offending hydrogen is instead a methyl group. The thioacetal **20** however could not be lithiated either.[155] Also, the Grignard was inaccessible precluding its use in the benzhydrol synthesis in place of lithiated **20** in condensation with ethyl formate.



Scheme 2.7. Synthesis of a thioacetal analog to circumvent acetal hydrolysis.

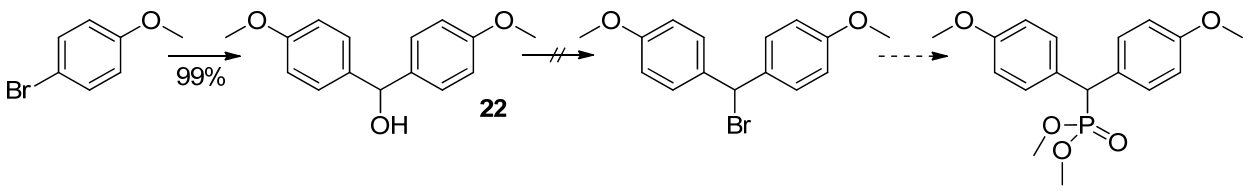
A final attempt to prepare the thioacetal protected benzhydrol was made as shown in Scheme 2.8. The commercially available 4-bromobenzaldehyde dimethyl acetal was used in the synthesis of benzhydrol **21** with plans to convert this to the thioacetal analog. Conditions for transthioacetalization with magnesium bromide[156] did cleave the dimethyl acetal, however, none of the dithiol reacted to furnish the thioacetal. Protection of the dialdehyde **15**, also failed to yield the desired product.



Scheme 2.8. A alternative route to a thioacetal-protected monomer.

Reagents and Conditions: (a) i) *n*-BuLi, hexanes, THF, -78°C, ii) ethyl formate, THF, warm to RT, 95%; (b) TsOH, H_2O, acetone, 99%.

The phosphonate monomer **11** had proven more challenging to prepare than practical, however the dialdehyde component **13** was excellent as a stable, easily-accessible solid. Therefore, a replacement for the former monomer was sought. With no suitable way to mask the carbonyls, their use as a peripheral group was abandoned completely. Much more chemically robust, yet still suitable for later functionalization of the dendrimer was a methyl ether as was used in the first synthesis of phenylene vinylene dendrons described earlier. It was hoped that the dendrimers could be synthesized using the initially envisioned mild bromination conditions for direct conversion of TBS ethers (using PPh_3Br_2) followed by treatment with trialkylphosphite to yield the phosphonate. This synthetic pathway would have been advantageous in reducing the number of transformations necessary in between dendron growth reactions.



Scheme 2.9. A methoxy-substituted phosphonate would lead to dendrons with identical substitution to the first method.

Using now-familiar conditions, the benzhydrol **22** was prepared from 4-bromoanisole. Preparation of the bromide was not as easily accomplished, and what little product might have been formed as indicated by TLC was not isolable. The difficulties in preparation of the benzhydryl bromide was attributed to the strong donating nature of the methyl ethers making for a highly stabilized benzhydryl cation that was overly susceptible to hydrolysis. This alternative would not be suitable either. Having demonstrated the extended π conjugation in a second series of *p*-phenylene vinylene dendrons, no further attempts at dendron synthesis were undertaken.

3.0 FUNCTIONALIZATION AND TESTING OF PPV DENDRONS

To test the ability of the prepared *p*-phenylene vinylene dendrons in a light harvesting application, functionalization of the periphery and core was necessary. In collaboration with Dr. Jung-Kun Lee's group, dye-sensitized solar cells were prepared. This platform would provide a set of established methods with which to test the dendrons and look for increased light-harvesting performance with increasing generation.

3.1 DYE-SENSITIZED SOLAR CELLS

Edmond Becquerel discovered the photoelectric effect and first reported it in 1839.[157] While new photoelectrochemical cells were developed over the next 160 years, interest in their advancement skyrocketed following the energy crisis of 1973 with over one thousand publications in the following decade.[158] Since then work has continued due to a realization for the necessity of developing alternatives to fossil fuels, especially in light of increasing energy demand across the planet. The sun represents an inexhaustible resource if technology is developed to efficiently harness the energy it delivers to the earth's surface.[159-162]

One type of photoelectrochemical cell is the dye-sensitized solar cell. The prototype of this type of cell was made by O'Regan and Grätzel in 1991.[163] For this reason, these devices are sometimes referred to as Grätzel cells. Dye-sensitization was an old concept that can be traced

to early photographic methods. Before 1991, attempts to use dye sensitization resulted in very low energy conversion. This was primarily a result of a belief that the smoother the surface of the semi-conducting layer, the better the cell would perform.[164] The amount of light a single layer of dye molecules could absorb though is less than 1%. O'Regan and Grätzel replaced the smooth semi-conducting layer with a thin layer of titanium dioxide nanoparticles which lead to a 2000-fold increase in surface area to which dye molecules could be chemisorbed. Their cells achieved 7.1% energy conversion efficiency. Recently, Grätzel et al. set a new record for this type of cell with a certified efficiency of 14.1%, while some cells tested in their lab measured over 15%.[165]

Dye-sensitized cells are attractive due to their ease of preparation relative to other cells, their inexpensive materials, and tolerance for impurities versus other cells, though impurities can reduce the lifetime of the cells.[160] Cells are prepared as a sandwich between two layers of glass each coated with a transparent conducting oxide (TCO), often indium tin oxide. On what will be the front side of the cell, the side facing the light source, most often a thin layer of anatase titanium oxide added. Nanoparticles of TiO_2 in a colloidal suspension are coated on the glass which is then sintered creating a network of TiO_2 with direct contact between the nanoparticles from 5-20 μm thick. The dye is then chemisorbed onto the nanoparticles. A second sheet of TCO glass, sometimes with an added layer to increase conduction such as platinum or graphene, is placed on top as the countereletrode. The last component necessary to complete the circuit is an electrolyte that will fill the space between the between the top and bottom layers.

When these components are all combined as shown in figure 3.1, the cell will function to convert light into energy. When a cell is exposed to light, the cycle begins by absorption of a photon by the dye leading to an excited state. Excited electrons are injected into the TiO_2

resulting in oxidation of the dye. The electrons then migrate through the TiO_2 to the front electrode. The energy is harnessed to do work external to the cell. Electrons are then returned to the cell via the counter-electrode. Triiodide is reduced to iodide at this electrode. The iodide/triiodide electrolyte completes the circuit when iodide is oxidized to triiodide and the oxidized dye is reduced to its original state.

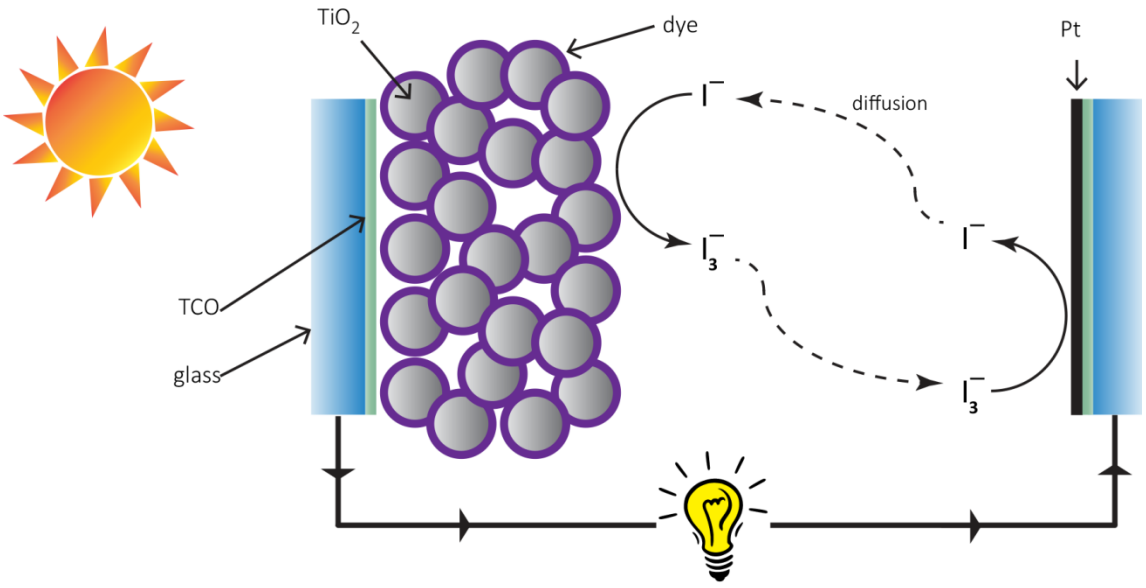


Figure 3.1. Representation of a dye-sensitized solar cell.

3.2 MODIFICATION OF THE DENDRONS

3.2.1 Design of Dendron-based Dyes

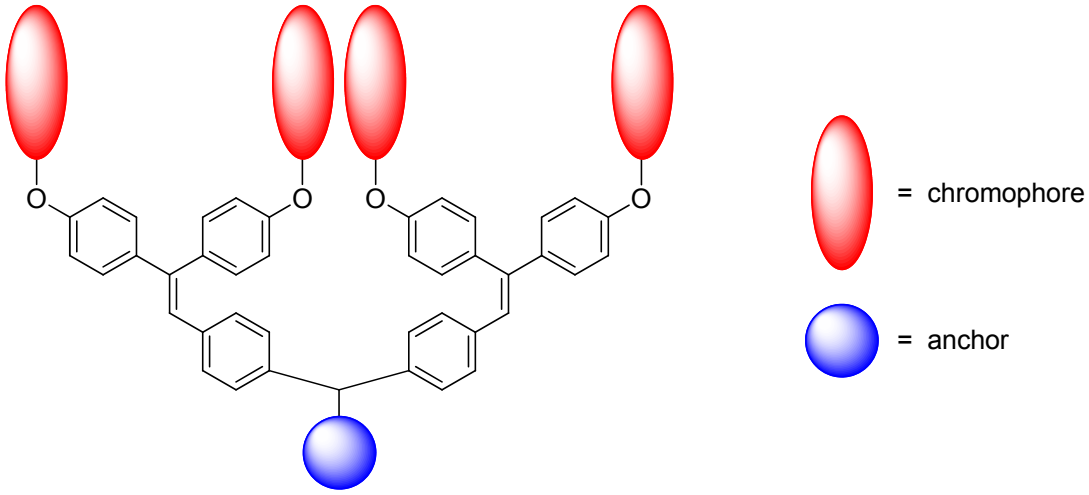
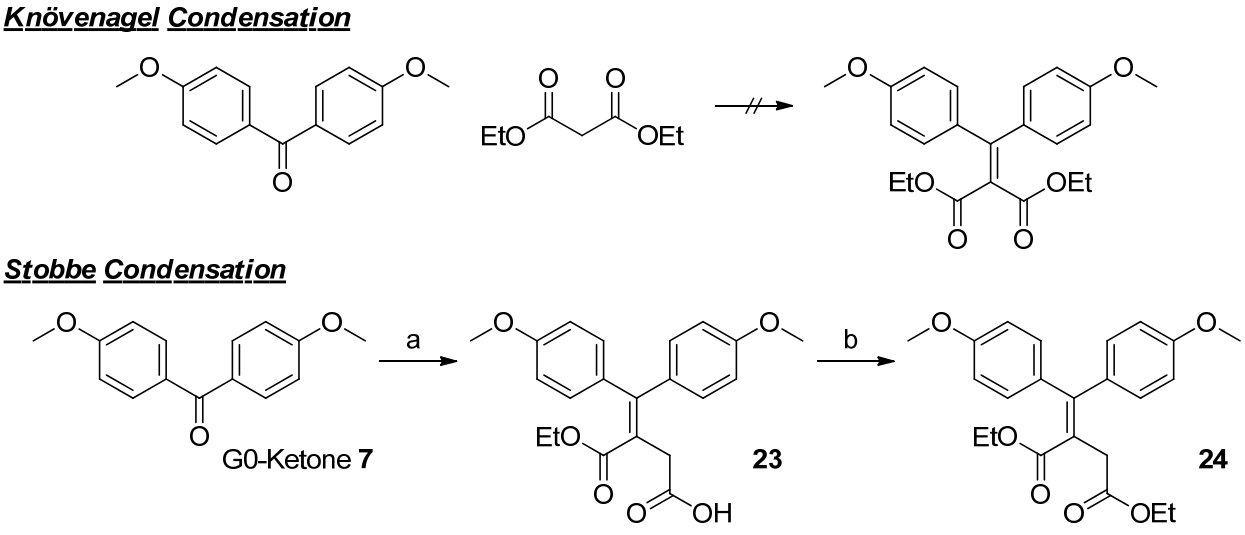


Figure 3.2. Basic design of dendron-based dyes.

In order to incorporate the dendrons into DSSCs, a dye was added to broaden and intensify the absorption of the compounds. Also, the apex of the dendrons were modified so that the dyes would adhere to the titanium oxide component of the DSSC. Porphyrins were chosen for the dye due to their previous use in solar energy applications, specifically solar hydrogen production.[166-179] They have also been used previously in dye-sensitized solar cells,[180-190] in one instance achieving over 12% efficiency.[191] Porphyrins are also amenable to modifications to increase solubility without meaningful changes to their photoproperties. Lastly, they are easily modified in a fashion that would allow them to be attached to the dendrons.

3.2.2 Synthesis of Dendron-based Dyes

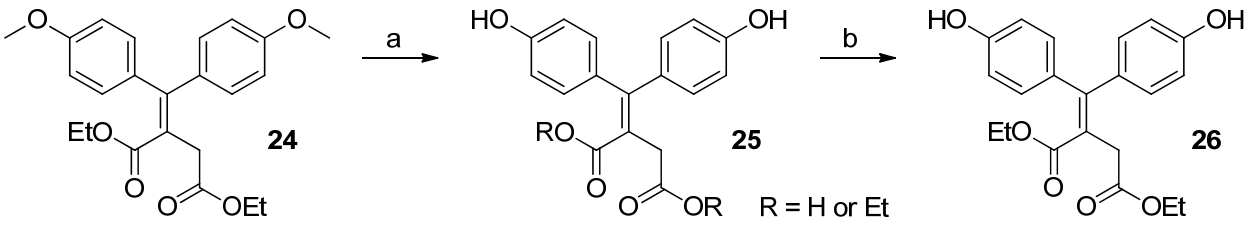
The apex of the dendrons was first modified in order to provide an anchor for the dendron to associate with the titanium oxide of the DSSC. 1,3-Dicarboxylic acids are often used. The Knövenagel condensation with diethyl malonate would yield a diester extending the conjugation of the π system of the dendrons. The esters could later be easily saponified furnishing the desired anchor. Benzophenones and diarylketones, however, are extremely poor substrates for the Knövenagel, even more so considering the methoxy groups present. Stobbe condensations of benzophenones with dialkyl succinate do have precendence however. Using the 4,4'-dimethoxybenzophenone as a model substrate, potassium *tert*-butoxide was added to a solution of benzophenone and diethyl succinate.



Scheme 3.1. Functionalization of the core ketone group.

Reagents and Conditions: (a) diethyl succinate, KO*t*Bu, THF, reflux; (b) ethanol, cat. H_2SO_4, reflux, 78% (over two steps).

Following the condensation, the free acid **23** was immediately esterified to aid in isolation of diester **24** and because it was found the following step proceeded more smoothly without the carboxylic acid present. Demethylation of the ethers, in preparation for attachment of the porphyrins, was accomplished with BBr_3. Treatment of ether **24** with BBr_3 did lead to some hydrolysis of the esters. Therefore, the crude phenol **25** was subjected to Fischer esterification to consolidate the mixture to a single compound. The G1-Ketone **9** was converted to a diester in the same fashion.

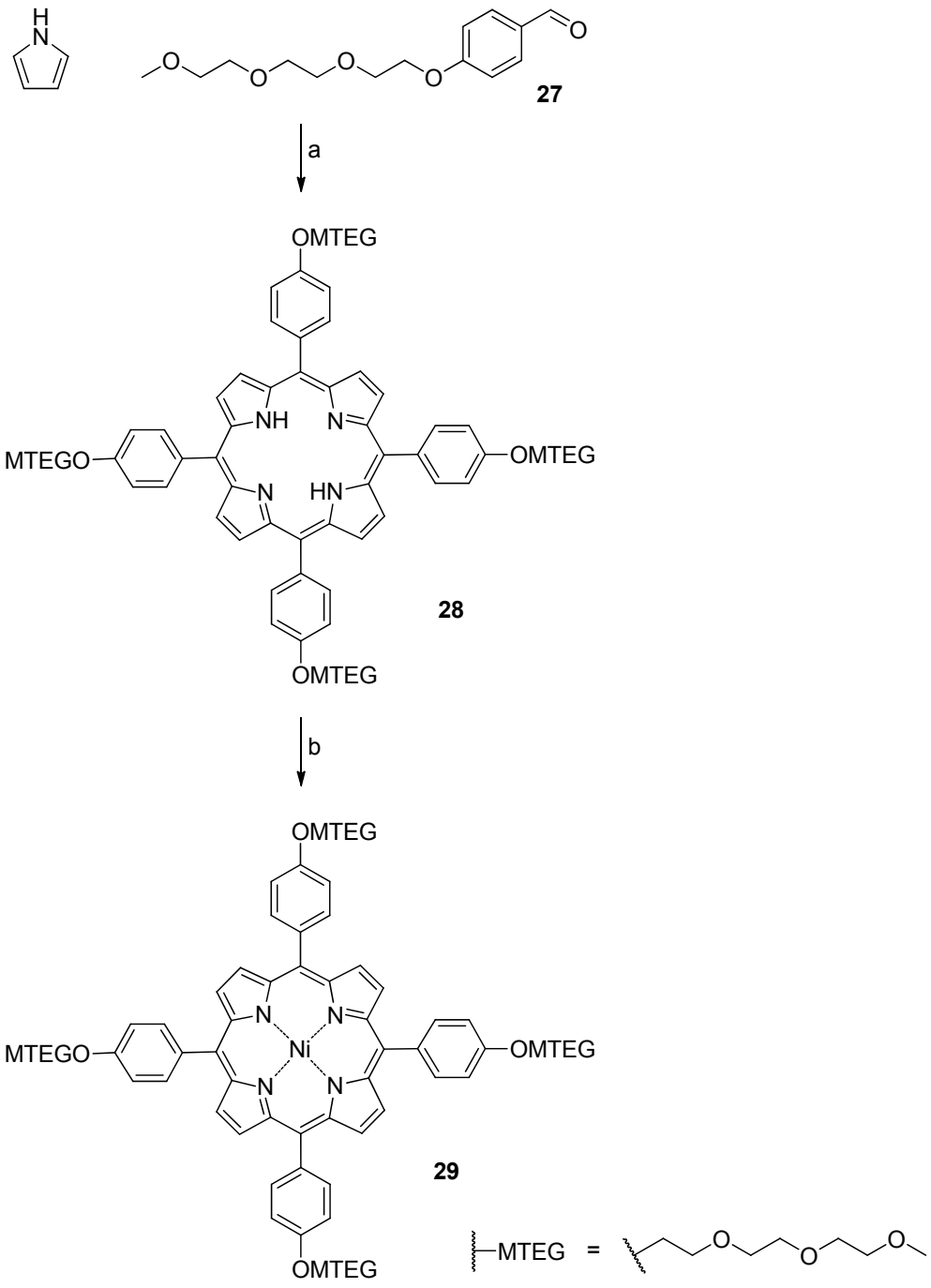


Scheme 3.2. Deprotection of the phenols in preparation for porphyrin attachment.

Reagents and Conditions: (a) BBr_3, CH_2Cl_2, -78 °C to RT; (b) ethanol, cat. H_2SO_4, reflux, 68% (over two steps).

With dendrons prepared, attention was turned to the porphyrins that would be needed. Porphyrins used in light-harvesting applications are most often variations of *meso*-tetraphenylporphyrin. This porphyrin suffers from low solubility and so often any modifications made are in an effort to increase their solubility. It was decided that short triethylene glycol units would be utilized to increase the solubility of porphyrins making them easier to handle and also to avoid any additional solubility issues that might arise once multiple porphyrins were attached to the dendron's periphery. To introduce these units into the porphyrin structure, aldehyde **27** was prepared for use in the porphyrin synthesis by reaction of 4-hydroxybenzaldehyde with

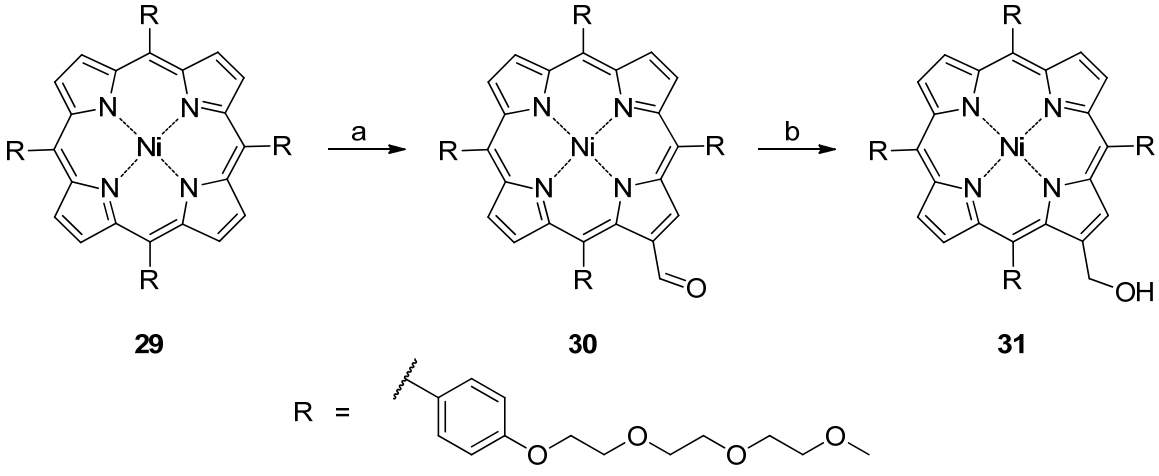
triethylene glycol monomethyl ether tosylate. Following the Lindsey protocol,[192] condensation of pyrrole with **27** in the presence of catalytic $BF_3 \cdot OEt_2$ followed by oxidation with DDQ gave porphyrin **28** in 34% yield. The porphyrin was then metallated to prevent unwanted reactions during additional functionalization. Nickel was chosen after a survey of the literature showed its inclusion did not disrupt characterization by NMR.



Scheme 3.3. Porphyrin synthesis and metallation.

Reagents and Conditions: (a) i) $BF_3 \cdot OEt_2$, $CHCl_3$, ii) DDQ, 34%; (b) $Ni(OAc)_2$, $CHCl_3$:MeOH (2:1), 90%.

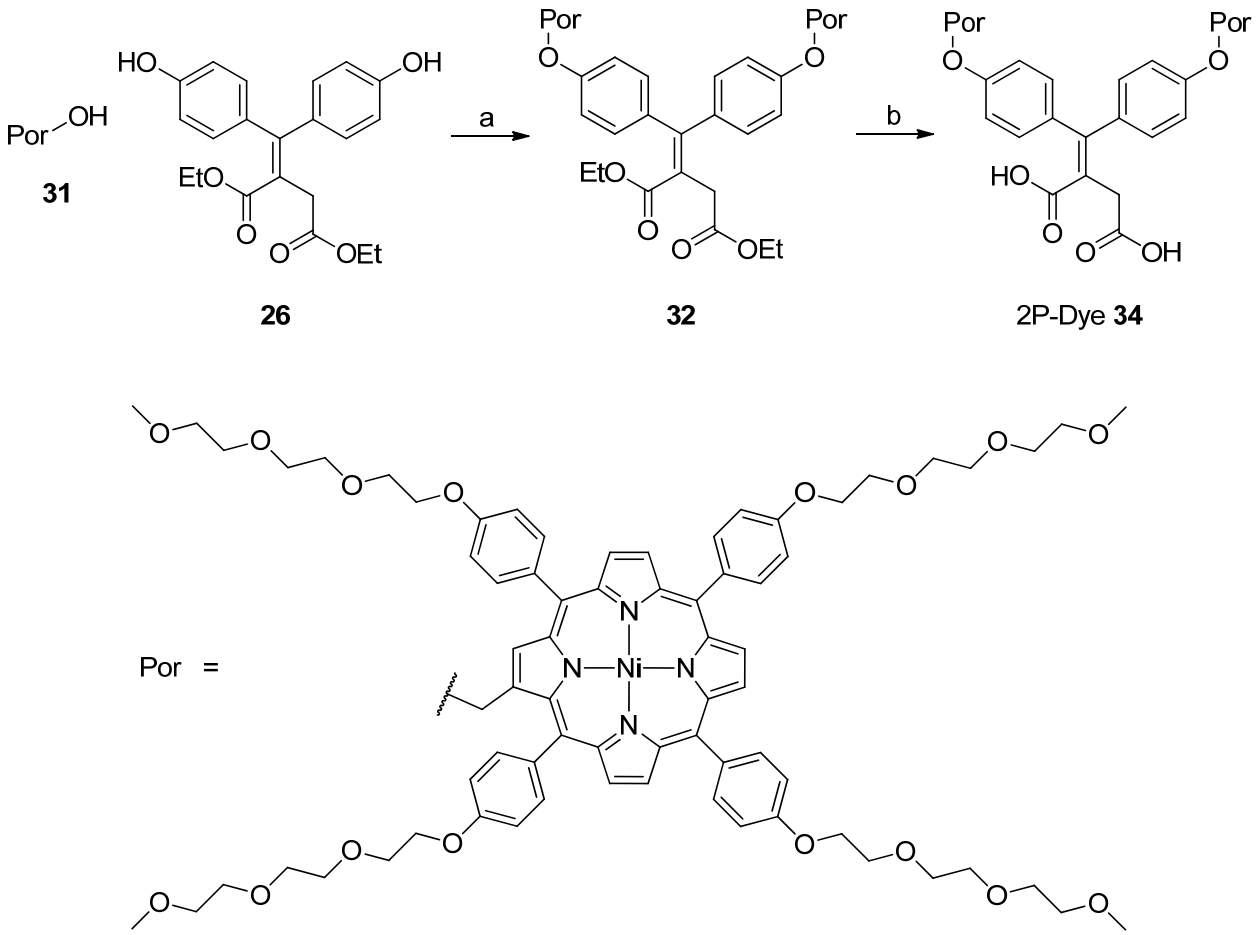
In anticipation of attaching the porphyrins to the dendrons by a Mitsunobu reaction, the porphyrins would require the addition of an alcohol group. Formylation of the porphyrin **29** was accomplished using Vilsmeier-Haack conditions. Reduction with sodium borohydride gave the required alcohol **31**.



Scheme 3.4. Preparation of the porphyrins for attachment to dendrons.

Reagents and Conditions: (a) $POCl_3$, *N,N*-dimethylformamide, 1,2-dichloroethane; (b) $NaBH_4$, $CHCl_3$:MeOH (4:1), 91% (over two steps).

The porphyrin-dendron conjugates were prepared using a Mitsunobu reaction as shown in Scheme 3.5. Saponification of the esters gave the final porphyrin-dendron-diacid compounds that would be tested as dyes. A final compound in the series, 1P-Dye **33** was prepared from 4-hydroxybenzaldehyde to give a single-porphyrin dye with similar structure to the others with two and four porphyrins each as shown in Figure 3.3.



Scheme 3.5. Representative preparation of a dye shown for 2P-Dye **34**.

Reagents and Conditions: (a) DIAD, PPh_3, THF, 0 °C to RT; (b) 1M $NaOH_{(aq)}$, THF, reflux, 27.2% (over two steps).

3.2.3 Characterization of the Dendron-based Dyes

UV-visible absorption spectra of each of the dyes were recorded. Shown in Figure 3.3 are the spectra adjusted to a common concentration. Demonstrating the increasing number of porphyrin moieties, the absorption of each dye nearly doubles as the number of porphyrin chromophores doubles. However, a first generation dendron with three porphyrins attached would give a similar value to the dendron with four porphyrins once the change in concentration based on the different molecular weight has been taken into account. Another way of judging the number of porphyrins per dye is possible for this compound. The 4P-Dye **35** also has an absorbance attributed to the first generation phenylene vinylene dendron at 333 nm similar to the other dendrons of this generation that had been prepared. Using this absorbance as an internal standard of molar absorbtivity, the ratio of porphyrin to dendron is also estimated to be four to one in that compound. NMR spectroscopy was not used in characterization as the signals were too broad to provide useful information.

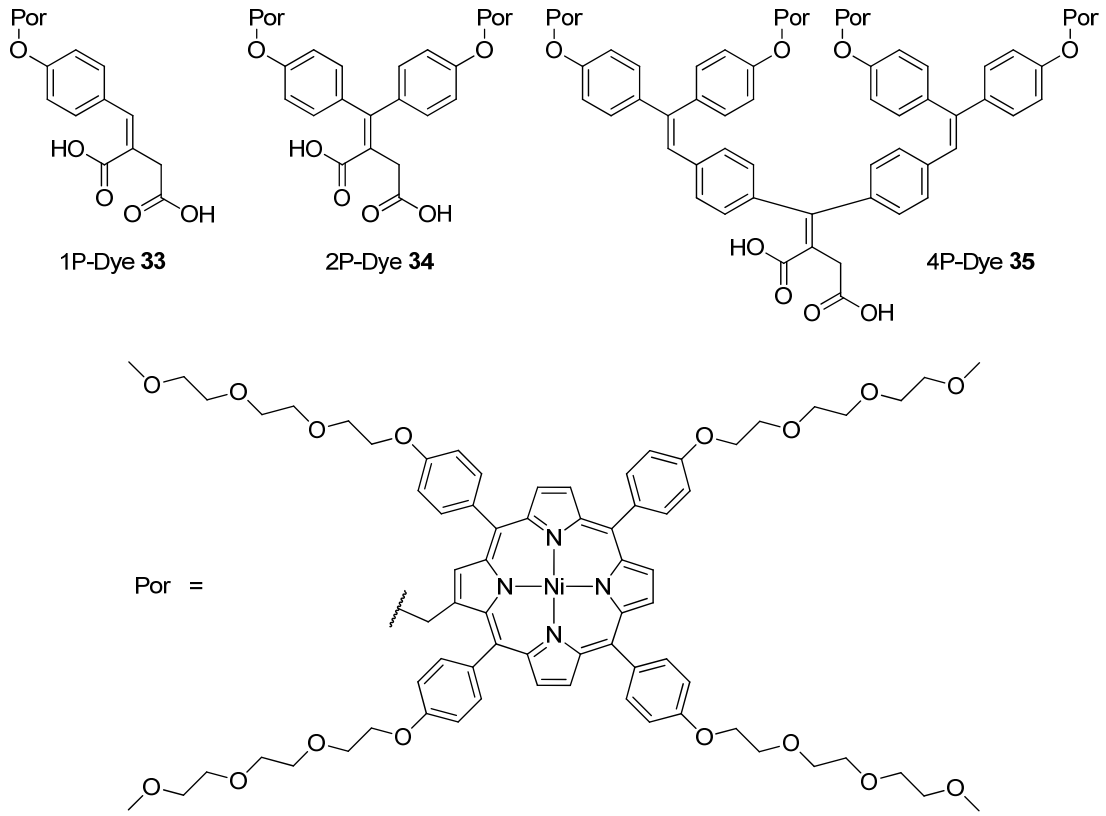


Figure 3.3. Structures of prepared dyes.

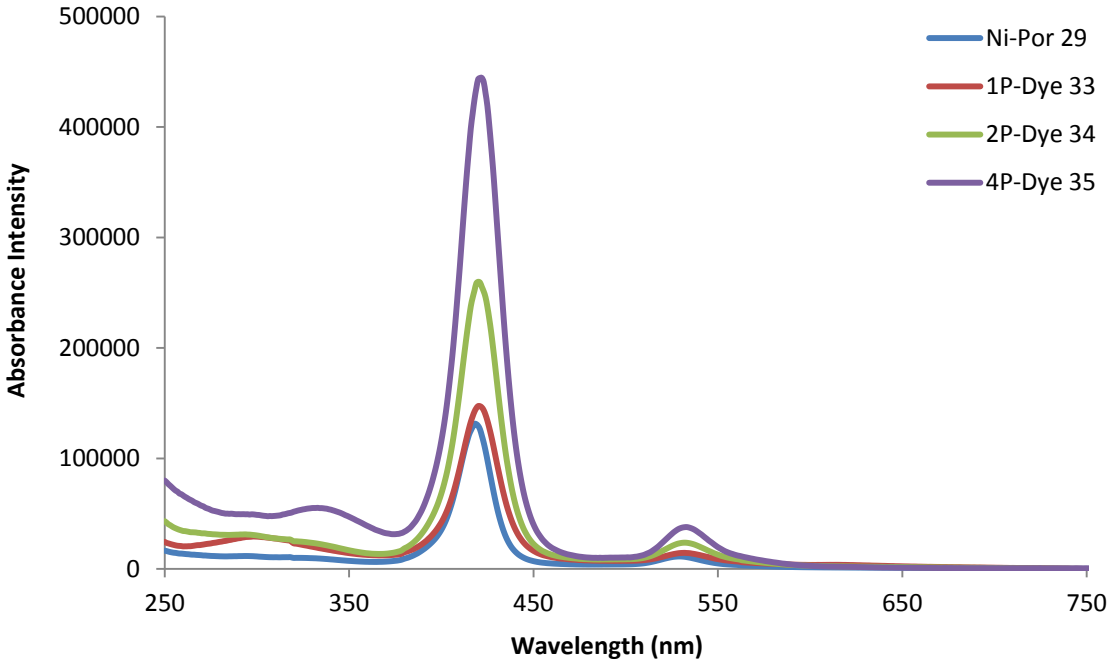


Figure 3.4. UV-Vis absorption spectra adjusted to reflect a common dye concentration.

Experimental Conditions: Collected in dichloromethane. [Ni-Por **29**] = 9.3 x 10^{-6} M; [1P-Dye **33**] = 3.8 x 10^{-6} M; [2P-Dye **34**] = 4.7 x 10^{-6} M; [4P-Dye **35**] = 2.7 x 10^{-6} M. Spectra adjusted to a common concentration of 0.5 M.

Table 3.1. UV-Vis absorption data for dyes.

Compound	λ_{max} (nm)	ϵ ($L \cdot mol^{-1} \cdot cm^{-1}$)
Ni-Por **29**	418	262,581
	529	22,500
1P-Dye **33**	420	294,754
	532	29,034
2P-Dye **34**	420	519,727
	532	47,435
4P-Dye **35**	333	110,506
	421	888,772
	533	75,714

All spectra collected in dichloromethane.

The synthesis of 1P-Dye **33** was supported by high resolution mass spectrometry. Using electrospray ionization, this compound was identified by the $[M+2Na]^{2+}$ peak at m/z 799. Switching to negative ionization the singly charged $[M-H]^-$ peak at 1551 was also found. HRMS of the larger dyes failed to yield molecular ion peaks matching 2P-Dye **34** or 4P-Dye **35**. The two porphyrin dye did show a peak in the correct region. At 2955 m/z a strong signal was observed. 2P-Dye **34** however should have measured 2978. With 4P-Dye **35**, electrospray ionization proved ineffective at producing ions of the parent compound as well as MALDI. These techniques did result in ionization of the porphyrins cleaving the C—O benzyl-type bond.

Elemental analysis of the dyes was completed for 2P-Dye **34** and 4P-Dye **35**. Because these compounds have a very repetitive structure, the elemental composition from one to the next, or between a dye that had incomplete reaction with the porphyrin, does not change much. However, a comparison of the results to the expected value for complete reaction versus expected values for incomplete reactions yields greater error as porphyrins are removed as shown in Table 3.1. The data best fit the expected dyes with two and four porphyrins each for 2P-Dye **34** and 4P-Dye **35** respectively.

Table 3.2. Elemental analysis of 4P-Dye **35** compared to calculated values of related products with fewer porphyrins.

# of Porphyrins		4		3		2		1	
Chemical Formula		$C_{337}H_{370}N_{16}Ni_4O_{72}$		$C_{264}H_{286}N_{12}Ni_3O_{56}$		$C_{191}H_{202}N_8Ni_2O_{40}$		$C_{118}H_{118}N_4NiO_{24}$	
Element	**Found**	**Calc'd**	**Δ**	**Calc'd**	**Δ**	**Calc'd**	**Δ**	**Calc'd**	**Δ**
C	66.6	*67.11*	-0.51	*67.48*	-0.88	*68.13*	-1.53	*69.65*	-3.05
H	6.11	*6.18*	-0.07	*6.13*	-0.02	*6.05*	0.06	*5.84*	0.27
N	3.59	*3.72*	-0.13	*3.58*	0.01	*3.33*	0.26	*2.75*	0.84
Ni	3.76	*3.89*	-0.13	*3.75*	0.01	*3.49*	0.27	*2.88*	0.88

3.3 TESTING OF THE DYES

The porphyrin-dendron conjugates were shared with our collaborators for testing by incorporation into dye-sensitized solar cells. Unfortunately, the dyes performed very poorly. The incident photon to current efficiency graph shows the lack of current generated by absorptions from the synthesized dyes in Figure 3.4. The dyes transferred so little charge that the current that was produced by the cell was dominated by absorptions from the titanium oxide. This feature is often not observed as a dye that performs well will be at least 20 times stronger than this absorption.

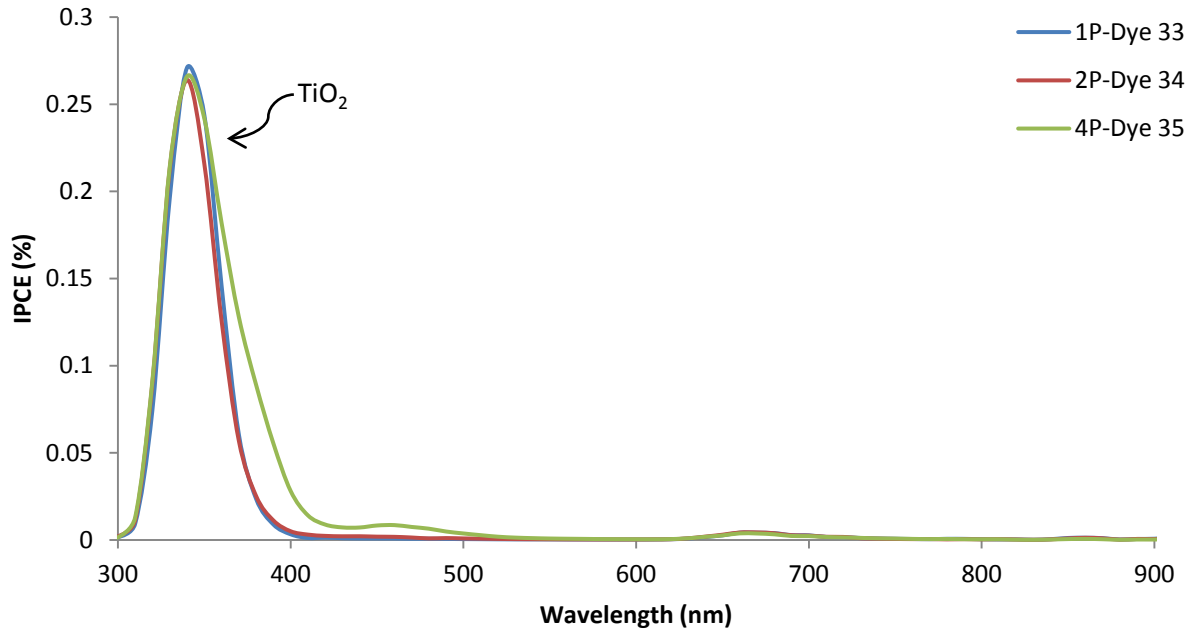


Figure 3.5 Incident photon to current efficiency of the dye compounds.

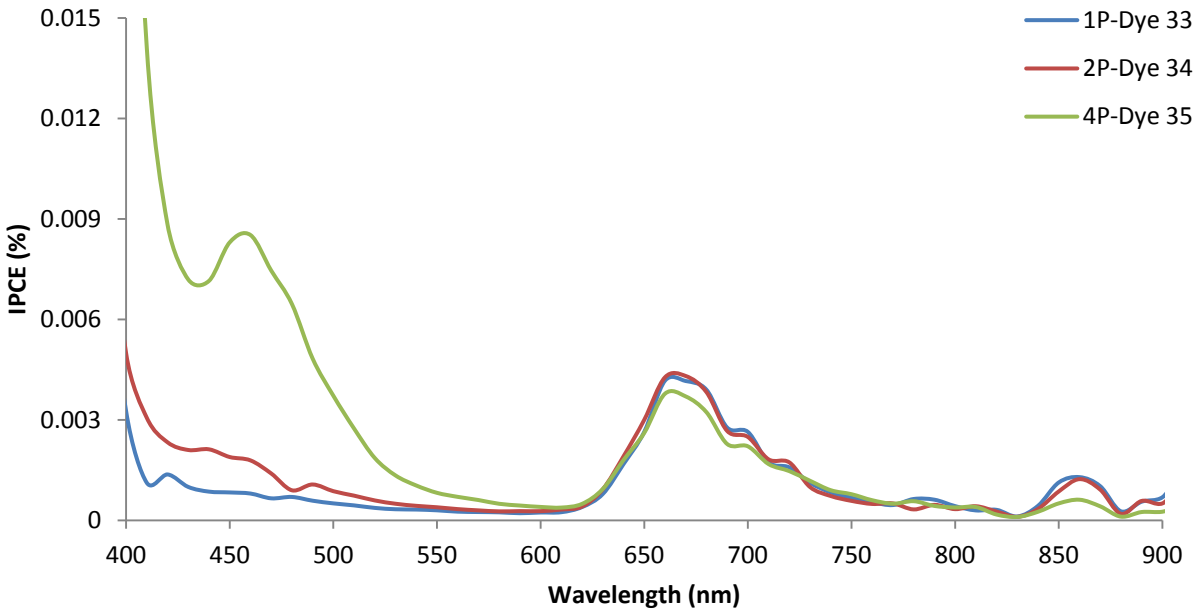


Figure 3.6. Incident photon to current efficiency of the dye compounds focusing on 400-900 nm region.

Closer inspection of the region between 400 and 900 nm , Figure 3.6, does show some activity. Between 400 and 500 nm the 4P-Dye **35** delivers a higher photon to current efficiency than the 2P-Dye **34**, which in turn is more active than 1P-Dye **33**. This region is on the shoulder of the Soret band at 420 nm seen in Figure 3.4 and absorbance at these wavelengths is very weak. A second region around 650-700 nm does not correspond to any absorptions measured in either the UV-vis absorption spectra of the dyes, porphyrin, or the dendrons. To more conclusively determine the relative activity of the dendron-dye conjugates, a more active system is necessary.

One explanation for the disappointing performance of the dendritic dyes is related to the nickel porphyrins used as the peripheral chromophores. Nickel porphyrins do not have a significantly different absorption spectrum compared to either the free base porphyrins or differently metallated porphyrins.[193] The luminescence spectra of porphyrins however does change, in some cases dramatically, with changes of the metal complexed within the porphyrin. In the case of nickel porphyrins, fluorescence cannot be observed. Instead, they undergo a non-radiative decay process extremely quickly, faster than 10^{10} s^{-1}.[194] This being the case, nickel porphyrins are unsuitable for light harvesting applications.

The fluorescence spectra of the dye compounds show the effects of the nickel porphyrins as well. The excitation spectra of the three dyes (**33-35**) and nickel porphyrin **29** are shown in Figure 3.5. Each spectrum shows a total lack of fluorescence when excited in the region around the absorption maximum of 420 nm of the dyes. The emission spectra show an inner filter effect of the nickel porphyrins. Each exhibits a trough of no fluorescence centered at the absorption maxima of the dyes. The nickel porphyrins act as a filter absorbing any fluorescence energy at these wavelengths.

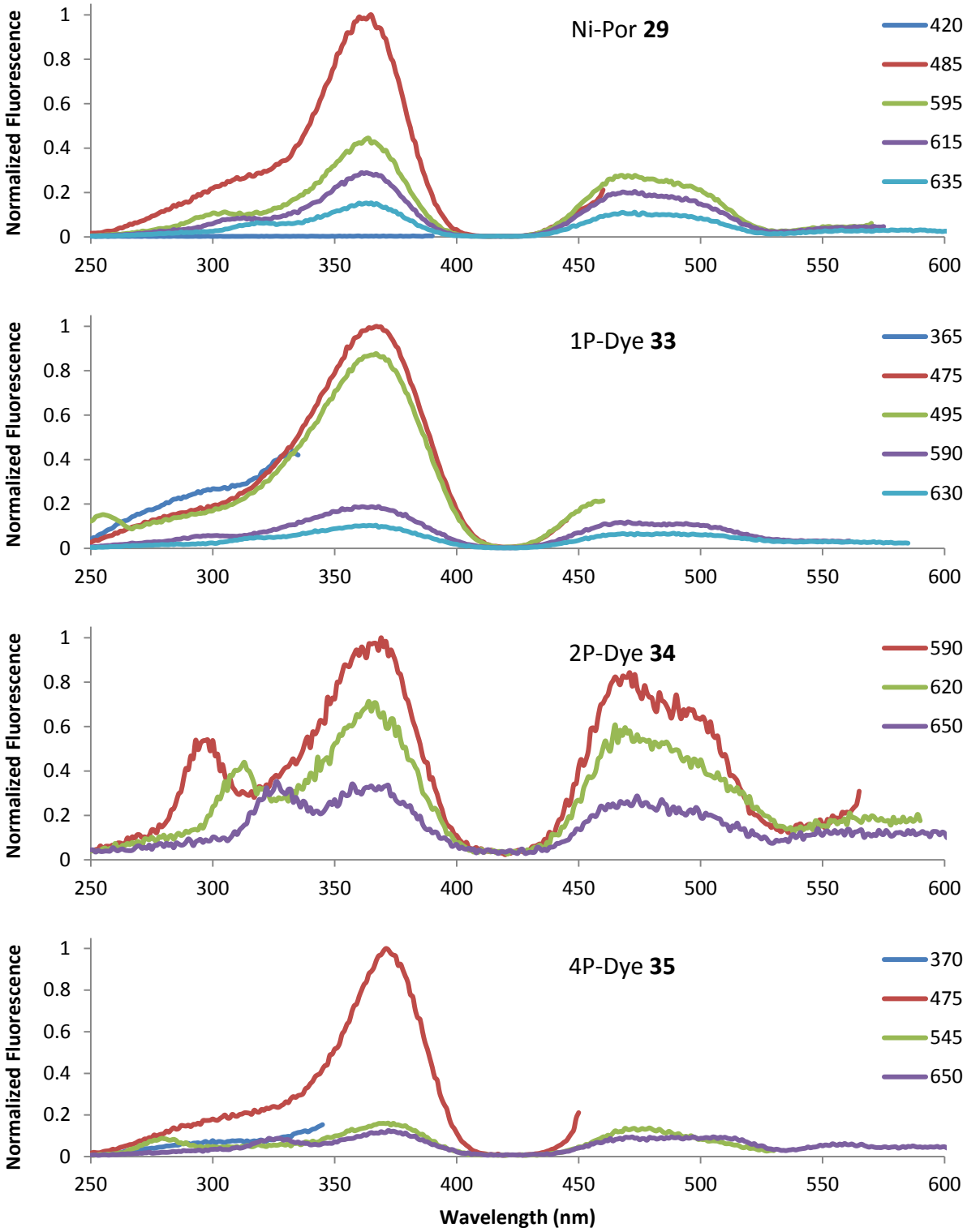


Figure 3.7. Normalized fluorescence excitation spectra of porphyrin **29** and dyes **33-35** as observed at wavelengths shown in legends. All spectra were recorded as dichloromethane solutions of ~10^{-6} M.

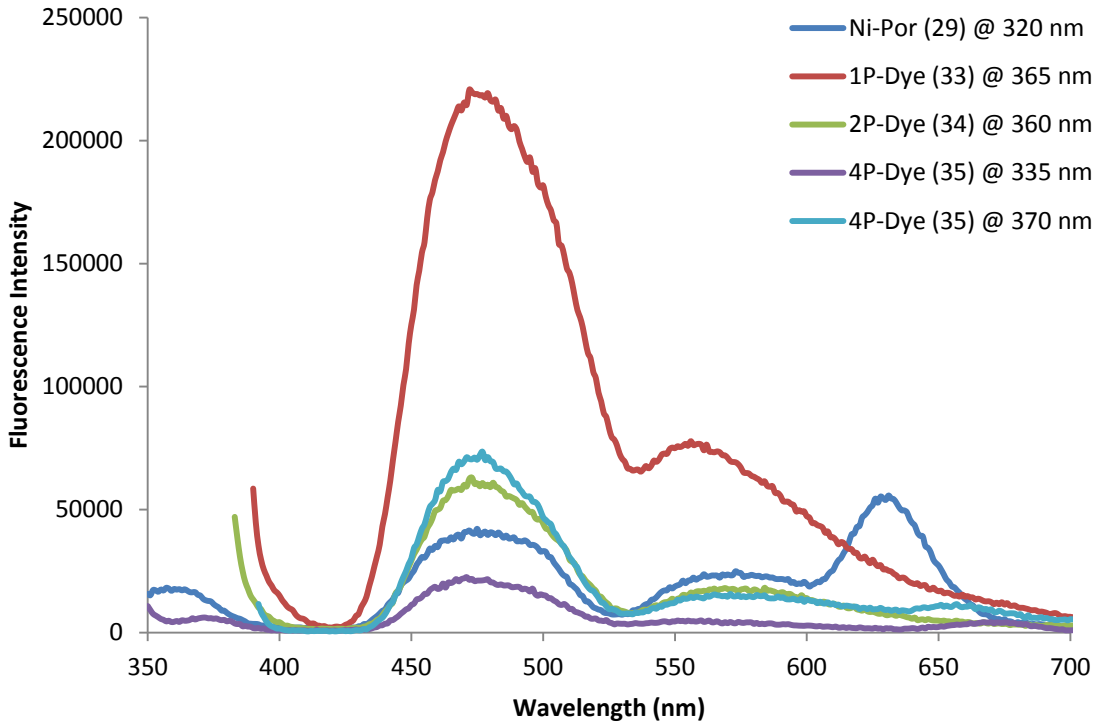


Figure 3.8. Fluorescence emission spectra (excitation wavelengths in legend) demonstrating the inner filter effect of the nickel porphyrin chromophores centered at 420 nm.

Other factors may also have contributed to a lower efficiency for dyes based on this system. There is a not a completely conjugated pathway between the donors and the core of the dendrimer. The ether connection at the periphery represents a break in the π system. This however might also have been beneficial by retarding charge recombination. It is also unknown what interactions exist between the dyes. Energy transfer between the dyes forming a shell of a dendrimer has been shown to be beneficial. This would be analogous to energy transfer in the natural photosynthetic unit, and the effect has been observed previously.[49, 71] In those systems though, when the shell was not complete, efficiencies dropped drastically. As the dyes prepared are only dendron wedges, this may be observed in this system as well.

4.0 CONCLUSIONS

The dyes prepared from the nickel porphyrins were ineffective when incorporated into dye-sensitized solar cells. Therefore, the question remains of the potential that *p*-phenylene vinylene dendrons acting as bridges between multiple donors and an acceptor might have. A number ideas for new experiments have been prompted by this work with these dendrons.

The most basic change that could be made to the system would be replacement of the nickel in the porphyrins with zinc. Zinc porphyrins have none of the issues with fluorescence, energy or charge transfer that their nickel counterparts possess. Zinc porphyrins have been used in many light-harvesting applications and so their inclusion in this system would be a minor change that could help to determine if any increase in efficiency is with the dendritic system.

More fundamental experiments would involve learning more about the energy transfer in the *p*-phenylene vinylene system. Attachment of dyes more suitable to studying this effect would allow a better understanding of whether the energy is transferred via the dendrons or not. Dyes such as the coumarins used by Fréchet[52] in early examples of light-harvesting dendrimer or the series of polycyclic aromatic imides used by Müllen[64] would be potential options.

These same alternate chromophores could be used in testing in the dye-sensitized solar cell platform as well. While these would not be good dyes for overall light to energy conversion due to their limited, narrow absorptions, they would be suitable to investigating the changes to efficiency in relation to dendron generation. Once that process is better understood, the

incorporation of ruthenium dyes more commonly used in dye-sensitized solar cells could provide a broad absorption cross-section that would be ideal in such a system.

In another variation, a strong electron acceptor such as a viologen could be placed at the focus of the dendrons. Electron transfer through the dendrons could be tested then as well. Porphyrins and viologens were two early components in many solar hydrogen systems. Electron transfer from porphyrin to viologen is well known. Electron transfer from benzyl ether dendrons, not a particularly good chromophore, to viologen has been reported before as well.[69] A porphyrin-dendron-viologen conjugate might be especially useful for photoinduced water splitting.

Changes to the dendron also pique interest. Addition of electron donor groups to the benzhydryl units towards the periphery and electron withdrawing groups closer to the core would create an energy gradient within the dendron. This gradient would help to funnel energy absorbed by whatever chromophores were attached from the periphery to the focus.

The periphery of the dendrons also has potential to be changed. In the current system, the ethers were a robust group for dendron synthesis. However, once the porphyrins were attached, the ethers were the only break in π conjugation between the porphyrins and the core group. The use of alternate functional groups that would leave a complete pathway of conjugation between donor and acceptor would be beneficial to the rate of charge separation if the dendron bridge is used in electron transfer. The break however might also provide a barrier slowing down charge recombination. In one possibility, the periphery of the dendrons could have alkyne functional groups. Once the dendrons are synthesized, the peripheral alkynes would allow functionalization of the periphery by click chemistry with groups containing an azide. The resulting connection between dendron and peripheral group would extend the conjugation of the dendrimer to the

attached group. The break however might also provide a barrier slowing down charge recombination.

Lastly, from the X-ray crystal structure that was obtained from the first generation dendron it is known that some minor twisting of the branches occurs. This is not enough to disrupt conjugation. The twisting though does lead to poorer conjugation of the branches. The replacement of the benzhydryl units with a fluorene derived unit would minimize the twisting. A fluorene-based dendrimer would be a particularly rigid structure.

Ultimately, there is still much to be studied with *p*-phenylene vinylene dendrons. Between the organometallic route of Itami and coworkers,[143] and the Horner-Wadsworth-Emmons based approach developed in this work and repeated by Imaoka, Ueda, and Yamamoto,[144] multiple pathways now exist to access these dendrons. Hopefully their utility in charge transfer is further explored in the not too distant future.

5.0 EXPERIMENTAL INFORMATION

5.1 GENERAL TECHNIQUES

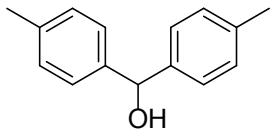
All moisture-sensitive reactions were performed under an N_2 atmosphere under anhydrous conditions unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium-benzophenone or purchased anhydrous and used without further purification. Dimethylformamide (DMF) was distilled from P_2O_5. All other solvents and reagents were used without further purification unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm EMD silica gel plates (60F-254) using UV-light (254 nm) to visualize and anisaldehyde, $KMnO_4$, or dinitrophenylhydrazine stains, or I_2 to develop. Flash chromatography was performed using silica gel (230-400 mesh) purchased from Sorbent Technologies. NMR spectra were recorded on Bruker Avance AM300 or AM500 instruments at room temperature. Chemical shifts (δ) are reported in parts per million, and the residual solvent peak[195] was used as an internal standard. Data are reported as follows: chemical shift, multiplicity, integration, and coupling constant. The following abbreviations are used to indicate the multiplicities: s, singlet; d, doublet; dd, doublet of doublets; app t, apparent triplet; m, multiplet; br, broad. IR spectra were obtained on a Nicolet Avatar 360 FT-IR E.S.P. spectrometer. UV-visible spectra were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer. Peak absorptions (λ_{max}) are reported in nanometers (nm). Molar absorbtivity

values (ϵ) are reported in units of $L \cdot mol^{-1} \cdot cm^{-1}$. Fluorescence emission and excitation spectra were recorded on a Jobin Yvon-Horiba Fluorolog-322 spectrofluorimeter.

Elemental analyses were performed by the Microanalysis Laboratory, University of Illinois in Urbana, Illinois.

Dye-sensitized solar cells were kindly prepared and tested by Bo Ding, Department of Mechanical Engineering & Materials Science, Swanson School of Engineering, University of Pittsburgh according the methods described in Ding et al.[196]

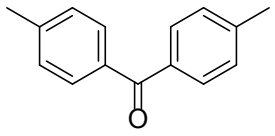
5.2 EXPERIMENTAL DATA



3

4,4'-Dimethylbenzhydrol (3). To a solution of 4-bromotoluene (66.812 g, 390.6 mmol, 2.05 eq.) in THF (250 mL) cooled to -78 °C was added *n*-butyllithium in hexanes (1.6 M, 250 mL, 400 mmol, 2.1 eq.) over three hours. After one hour ethyl formate (15.4 mL, 14.08 g, 190 mmol, 1.0 eq.) in THF (100 mL) was added dropwise. After two hours water (200 mL) was added and the reaction warmed to room temperature. The aqueous phase was extracted with diethyl ether (2 x 100 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product was used crude in the oxidation to **4**. A portion was recrystallized from hexanes to yield white needles for characterization. mp 69.0-70.2 °C; IR (film) 3294, 3024, 2921, 1614, 1511, 1451, 1037, 1020,

805, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, 4H, *J* = 8.0 Hz), 7.23 (d, 4H, *J* = 8.0 Hz), 5.77 (s, 1H), 2.80 (br s, 1H), 2.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.8, 128.9, 128.3, 75.6, 20.9; high resolution mass spectrum (EI+) calcd for $C_{15}H_{16}O$ (M^+) 212.1201, found 212.1210 *m/z*.

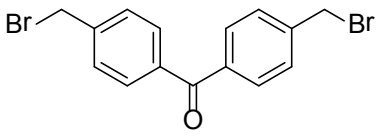


4

4,4'-Dimethylbenzophenone (4). To a solution of the crude alcohol **3** in dichloromethane (400 mL) cooled to 0 °C was added 1.0 M aqueous potassium bromide (20 mL, 20 mmol, 0.1 eq.) and TEMPO (0.304 g, 1.9 mmol, 0.01 eq.). Bleach, with 1.7 g $NaHCO_3$ added per 100 mL, was added in portions with vigorous stirring until a yellow-orange color persisted. The organic phase was washed with 10% HCl freshly prepared with 1.6 g potassium iodide added per 100 mL (200 mL), 10% aqueous $Na_2S_2O_3$ (200 mL), and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization from ethanol yielded **4** (30.053 g) as white needles. Flash chromatography of the mother liquor using 10% to 50% ethyl acetate in hexanes yielded additional **4** for an overall yield of 36.651 g (174.3 mmol, 91.7%). mp 91.0-92.5 °C; IR (film) 3040, 1649, 1607, 1408, 1277, 1177, 1116, 844, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 4H, *J* = 8.0 Hz), 7.26 (d, 4H, *J* = 8.0 Hz), 2.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 143.2, 135.6, 130.5, 129.2, 21.9; high resolution mass spectrum (EI^+) calcd for (M^+) $C_{15}H_{14}O$ 210.1045, found 210.1037 *m/z*.

Alternative one-step synthesis of **4,4'-dimethylbenzophenone (4).** 4-bromotoluene (27.92 g, 163.2 mmol, 1.02 eq.) was dissolved in THF (100 mL) in flame-dried flask. After cooling

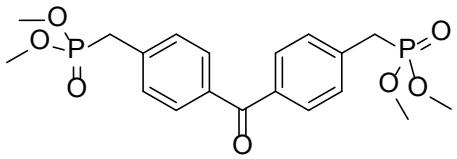
to -78 °C, *n*-butyllithium in hexanes (1.6 M, 100 mL, 160 mmol, 1.00 eq.) was added via cannula and the solution was stirred at -78 °C for one hour. A solution of *p*-tolunitrile (18.74 g, 160 mmol, 1.0 eq.) in THF (20 mL) was added via cannula at a rapid dropwise rate, pausing when the dry ice/acetone bath began bubbling vigorously indicating a rapid warming of the reaction mixture. After the addition was complete, the reaction was stirred two additional hours then quenched by the addition of saturated aqueous NH_4Cl. After warming to room temperature, the reaction mixture was extracted with diethyl ether (2 x 100 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$, filtered and concentrated. The crude mixture which contains both the desired product as well as the imine was then added to a solution of LiOH (~40 g, ~10 eq.) in methanol (125 mL) and water (100 mL) and refluxed for 36 hours until hydrolysis was complete. The mixture was cooled. Diethyl ether (100 mL), water (100 mL), and concentrated HCl (added until all solid was dissolved) were added and the layers separated. The aqueous layer was extracted with diethyl ether (2 x 50 mL), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL). After drying over $MgSO_4$, the solution was filtered and concentrated. Recrystallization from ethanol yielded **4** (30.70 g, 146 mmol, 91.2%) as white needles.



5

Bis(4-bromomethylphenyl)methanone (5).[197] To a solution of benzophenone **4** (49.384 g, 234.86 mmol, 1.0 eq.) in 1,2-dichloroethane (1000 mL) was added *N*-bromosuccinimide (84.02 g, 472.07 mmol, 2.01 eq.) and benzoyl peroxide (2.844 g, 11.74 mmol, 0.05 eq.). The solution

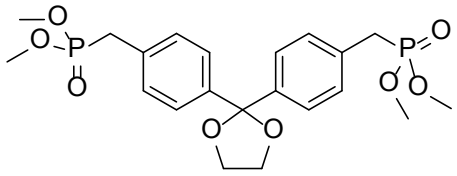
was heated to reflux for 120 minutes then allowed to cool slowly over night to allow succinimide to recrystallize. The succinimide was removed by filtration and the filtrate concentrated under reduced pressure. The resultant solid was dissolved in dichloromethane (200 mL) and washed with water (2 x 100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a light yellow solid (91.35 g). Analysis by NMR showed this solid to consist of the desired product **5** and trace amounts of succinimide and solvents. A small portion was recrystallized from dichloroethane with hexanes for characterization to yield **5** as a light yellow powder. mp 128.2-130.0 °C; IR (film) 3052, 2970, 1647, 1603, 1411, 1279, 1227, 1199, 1143, 927, 845, 771 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 4H, J = 8.0 Hz), 7.50 (d, 4H, J = 8.0 Hz), 4.53 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 142.2, 137.1, 130.4, 128.9, 32.122; high resolution mass spectrum (EI^+) calcd for (M^+) $C_{12}H_{12}O^{79}Br_2$ 365.9255, found 365.9237 *m/z*.



1

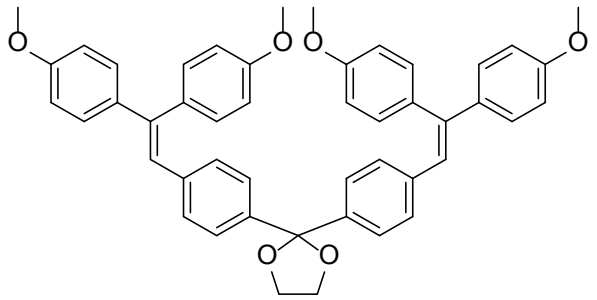
(4-[4-(Dimethoxyphosphorylmethyl)benzoyl]benzyl)phosphonic acid dimethyl ester (1).[198] To a solution of the crude dibromide **5** in toluene (125 mL) was added trimethyl phosphite (101.04 g, 814.3 mmol, 3.4 eq.). The mixture was refluxed for 6 hours before concentrating under reduced pressure. The resulting solid was washed with ethyl acetate to remove dimethyl methylphosphonate leaving **1** (43.066 g) as a light yellow powder. The washings were concentrated under reduced pressure and chromatographed using 5% methanol in dichloromethane to yield additional **1** for 61.506 g total (144.3 mmol, 61.4%, 2 steps). mp 126.5-128.0 °C; IR (film) 2955, 1651, 1607, 1416, 1252, 1181, 1053, 1028, 872, 788 cm^{-1}; ^1H

NMR (300 MHz, $CDCl_3$) δ 7.66 (d, 4H, J = 8.0 Hz), 7.33 (dd, 4H, J = 8.0 Hz, $^4J_{P\text{-}H}$ = 2.3 Hz), 3.62 (d, 12H, $^3J_{P\text{-}H}$ = 10.9 Hz), 3.15 (d, 4H, $^2J_{P\text{-}H}$ = 22.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 136.1 (d, $J_{P\text{-}C}$ = 9.2 Hz), 135.9 (d, $J_{P\text{-}C}$ = 2.9 Hz), 130.0 (d, $J_{P\text{-}C}$ = 2.6 Hz), 129.4 (d, $J_{P\text{-}C}$ = 6.5 Hz), 52.7 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 32.7 (d, $^1J_{P\text{-}C}$ = 137.0 Hz); high resolution mass spectrum (EI^+) calcd for (M^+) $C_{19}H_{24}O_7P_2$ 426.0997, found 426.0995 *m/z*.



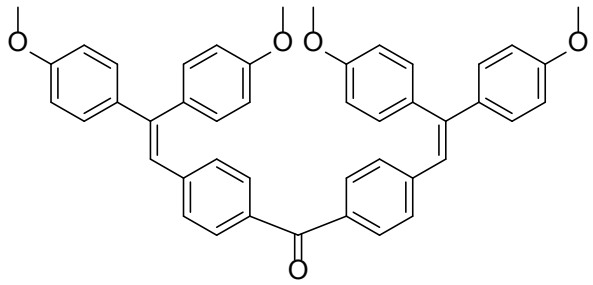
6

(4-(2-[4-(Dimethoxyphosphorylmethyl)phenyl]-[1,3]dioxolan-2-yl)benzyl)phosphonic acid dimethyl ester (6). To a solution of benzophenone **1** (1.203 g, 2.82 mmol, 1 eq.) in toluene (50 mL) was added ethylene glycol (5 mL) and *p*-toluenesulfonic acid (0.5 g). The mixture was refluxed in a Dean-Stark apparatus for 14 hours until water was no longer produced. The cooled reaction mixture was poured into 50 mL aqueous saturated $NaHCO_3$ solution. The separated organic phase was washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield **6** (1.166 g, 2.48 mmol, 87.9%) as a yellow powder. mp 89.8-94.5 °C; IR (film) 3032, 2956, 2895, 1609, 1509, 1463, 1417, 1247, 1179, 1019, 868, 788, 734 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, 4H, 8.1 Hz), 7.19 (dd, 4H, J = 8.1 Hz, $^4J_{P\text{-}H}$ = 2.3 Hz), 3.97 (s, 4H), 3.59 (d, 12H, $^3J_{P\text{-}H}$ = 10.8 Hz), 3.08 (d, 4H, $^2J_{P\text{-}H}$ = 21.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (d, $J_{P\text{-}C}$ = 3.2 Hz), 130.9 (d, $J_{P\text{-}C}$ = 9.0 Hz), 129.2 (d, $J_{P\text{-}C}$ = 6.5 Hz), 126.2 (d, $J_{P\text{-}C}$ = 2.6 Hz), 108.9, 64.6, 52.6 (d, $^2J_{P\text{-}C}$ = 6.7 Hz), 32.2 (d, $^1J_{P\text{-}C}$ = 137.6 Hz); high resolution mass spectrum (EI^+) calcd for (M^+) $C_{21}H_{28}O_8P_2$ 470.1259, found 470.1265 *m/z*.



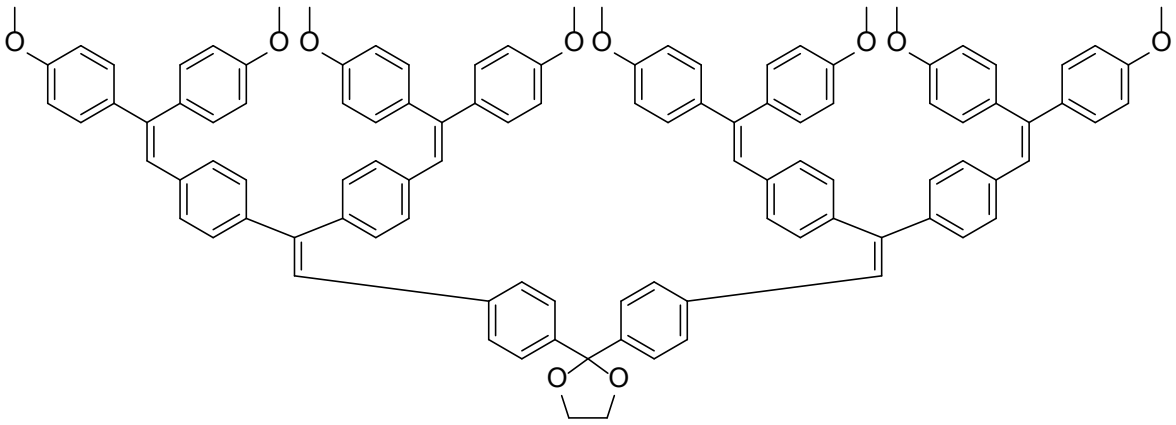
8

G1-Acetal (8). To a solution of phosphonate **6** (1.278 g, 2.72 mmol, 1 eq.) and 4,4'-dimethoxybenzophenone **7** (1.381 g, 5.70 mmol, 2.1 eq.) in DMF (10 mL) cooled to 0 °C was added in a dropwise fashion a solution of potassium *tert*-butoxide (1.219 g, 10.87 mmol, 4 eq.) in DMF (5 mL). The reaction was allowed to warm to room temperature over 12 hours then poured into water (20 mL). The mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic phases were then washed with 10% HCl (2 x 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 10% to 40% ethyl acetate in hexanes yielded **8** (1.315 g, 1.87 mmol, 68.8%) as a pale yellow solid. mp unsharp 82.0-120.0 °C; UV-vis (CH_2Cl_2) λ_{max} 328 nm (ε = 52,859), 236 nm (ε = 43,129); IR (film) 3032, 2999, 2954, 2895, 2835, 1604, 1572, 1510, 1463, 1284, 1246, 1174, 1081, 1034, 835, 737 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.26 (d, 1H, *J* = 8.7 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 8.6 Hz), 7.01 (d, 1H, *J* = 8.4 Hz), 6.89 (d, 1H, *J* = 8.6 Hz), 6.85 (d, 1H, *J* = 8.7 Hz), 6.84 (s, 2H), 3.97 (s, 4H), 3.84 (s, 6H), 3.80 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.7, 159.5, 142.5, 140.5, 138.0, 136.6, 133.0, 131.7, 129.4, 129.1, 126.1, 125.9, 114.4, 113.8, 109.4, 65.2, 55.6, 55.5; high resolution mass spectrum (EI^+) calcd for (M^+) $C_{47}H_{42}O_6$ 702.2981, found 702.3008 *m/z*.



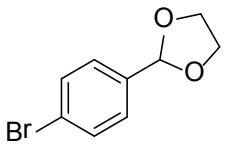
9

G1-Ketone (9). To a solution of the G1-Acetal **8** (1.305 g, 1.85 mmol, 1 eq.) in acetone (40 mL) was added water (3 mL) and *para*-toluenesulfonic acid (0.407 g). After one hour the reaction mixture was poured into ethyl acetate (50 mL) and washed with saturated aqueous $NaHCO_3$ (25 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography using 20% ethyl acetate in hexanes after loading the sample as a dichloromethane solution yielded **9** (1.218 g, 1.85 mmol, quantitative) as a bright yellow solid. Yellow needles formed in early fractions that were submitted for x-ray analysis. mp 171.5-172.2 °C; UV-vis (CH_2Cl_2) λ_{max} 370 nm (ε = 41,949), 285 nm (ε = 28,002), 250 nm (ε = 34,536); IR (film) 3034, 3001, 2955, 2906, 2835, 1648, 1593, 1572, 1510, 1463, 1282, 1247, 1178, 1033, 931, 833, 737 cm^{-1}; ^1H NMR (500 MHz, Acetone-d6) δ 7.51 (d, 4H, *J* = 8.3 Hz), 7.29 (d, 4H, *J* = 8.9 Hz), 7.17 (d, 4H, *J* = 8.3 Hz), 7.10 (d, 4H, *J* = 8.7 Hz), 6.98 (s, 2H), 6.95 (d, 4H, *J* = 8.7 Hz), 6.91 (d, 4H, *J* = 8.9 Hz), 3.83 (s, 6H), 3.81 (s, 6H); ^1H NMR (500 MHz, CD_2Cl_2) δ 7.54 (d, 4H, *J* = 8.2 Hz), 7.29 (d, 4H, *J* = 8.8 Hz), 7.13 (d, 4H, *J* = 8.2 Hz), 7.12 (d, 4H, *J* = 8.7 Hz), 6.91 (s, 2H), 6.90 (d, 4H, *J* = 8.7 Hz), 6.87 (d, 4H, *J* = 8.8 Hz), 3.83 (s, 6H), 3.82 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 195.3, 160.1, 159.8, 144.7, 142.6, 136.2, 135.6, 132.6, 131.9, 130.0, 129.5, 129.4, 125.3, 114.4, 113.9, 55.6, 55.5; high resolution mass spectrum (EI^+) calcd for (M^+) $C_{45}H_{38}O_5$ 658.2719, found 658.2696 *m/z*.



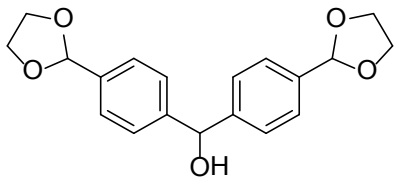
10

G2-Acetal (10). To a solution of the G1-Ketone **9** (0.528 g, 0.80 mmol, 2.2 eq.) and phosphonate **6** (0.171 g, 0.36 mmol, 1.0 eq.) in DMF (10 mL) cooled to 0 °C was added in a dropwise fashion a solution of potassium *tert*-butoxide (0.327 g), 2.9 mmol, 8 eq.) in DMF (10 mL). The solution was allowed to warm to room temperature overnight. Dichloromethane (20 mL) was added and the mixture was washed with 10% HCl (4 x 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 25% to 50% ethyl acetate in hexanes gave **10** (0.145 g, 0.09 mmol, 26.2%) as a pale yellow powder. mp unsharp 141.0-185.0 °C; UV-vis (CH_2Cl_2) λ_{max} 350 (ε = 114,016), 285 (ε = 56,294); IR (film) 3032, 2999, 2952, 2835, 1603, 1572, 1510, 1462, 1285, 1246, 1173, 1034, 833 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.27 (app t, 8H, *J* = 8.3 Hz), 7.23 (d, 4H, *J* = 8.4 Hz), 7.14-7.12 (m, 8H), 7.07 (d, 4H, *J* = 8.3 Hz), 7.03 (d, 4H, *J* = 8.0 Hz), 6.85-6.98 (m, 34H), 3.99 (s, 4H), 3.83 (s, 6H), 3.81 (s, 6H), 3.80 (s, 6H), 3.78 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.7, 159.5, 142.5, 142.4, 141.2, 141.0, 138.6, 137.7, 137.5, 136.7, 136.6, 133.1, 133.0, 131.9, 131.8, 130.1, 129.6, 129.5, 129.2, 129.1, 127.4, 127.3, 126.1, 126.0, 125.9, 114.4, 114.3, 113.9, 109.4, 65.3, 55.6, 55.5; high resolution mass spectrum (ES^+) calcd for ($M+H^+$) $C_{107}H_{91}O_{10}$ 1535.6612, found 1535.6636 *m/z*.



14

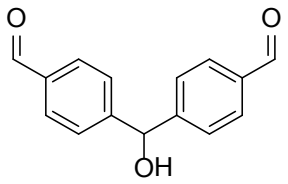
2-(4-Bromophenyl)-[1,3]dioxolane (14).[199] To a solution of 4-bromobenzaldehyde (40.826 g, 220.6 mmol, 1.0 eq.) in toluene (200 mL) was added ethylene glycol (24.6 mL, 27.39 g, 441.2 mmol, 2.0 eq.) and *p*-toluenesulfonic acid (0.84 g, 4.4 mmol, 0.02 eq.). The mixture was refluxed in a Dean-Stark apparatus for 24 hours until water was no longer produced. The cooled reaction mixture was poured into 100 mL aqueous saturated $NaHCO_3$ solution. The separated organic phase was washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The remaining yellow oil was vacuum distilled to yield **14** (47.712 g, 208.2 mmol, 94.4%) as a clear liquid that crystallized on standing as white needles. bp 113.5 °C @ 4 torr); mp 31.5-34.0 °C; IR (film) 3064, 2885, 1594, 1484, 1081, 1011, 816 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.55 (d, 2H, J = 8.4 Hz), 7.38 (d, 2H, J = 8.4 Hz), 5.76 (s, 1H), 4.14-3.95 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.9, 131.7, 128.7, 123.3, 103.3, 65.7; high resolution mass spectrum (EI^+) calcd for $C_9H_9{}^{79}BrO_2$ (M^+) 227.9786, found 227.9785 *m/z*.



12

Bis(4-[1,3]dioxolan-2-ylphenyl)methanol (11). A solution of **14** (32.419 g, 141.5 mmol, 2.03 eq.) in THF (100 mL) was cooled to -78 °C. 1.6 M *n*-Butyllithium in hexanes (90 mL, 144.0 mmol, 2.07 eq.) was added via cannula over 30 minutes. The solution was stirred an additional

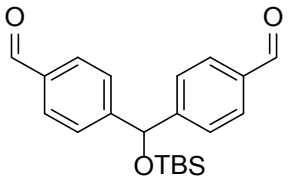
hour during which it became a cream color. Ethyl formate (5.62 ml, 5.15 g, 69.57 mmol, 1.00 eq.) in THF (50 mL) was added dropwise over 30 minutes. After one hour, the reaction was quenched with 200 mL of water then allowed to warm to room temperature. The aqueous layer was extracted with ether (2 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography using 25% to 50% ethyl acetate in hexanes as a stepped eluant yielded **11** (15.14 g, 46.1 mmol, 66.3%) as a white solid. mp 84.5-85.0 °C; IR (film) 3442, 2892, 1614, 1511, 1389, 1221, 1080, 819 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.42 (d, 4H, *J* = 8.2 Hz), 7.35 (d, 4H, *J* = 8.2 Hz), 5.76 (br d, 1H, *J* = 2.3 Hz), 5.74 (s, 2H), 4.09-3.94 (m, 8H), 2.97 (br d, 1H, *J* = 2.3 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 145.4, 137.7, 126.9, 126.7, 103.8, 75.7, 65.6; high resolution mass spectrum (ES^+) calcd for $C_{19}H_{20}O_5Na$ ($M+Na^+$) 351.1208, found 351.1198 *m/z*.



15

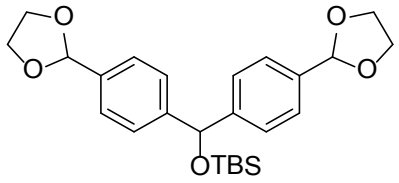
Alcohol 15. A solution of benzhydrol **23** (2.852 g, 8.6 mmol, 1 eq.), *para*-toluenesulfonic acid (163 mg), and water (5 mL) in acetone (40 mL) was stirred for 6 hours. The reaction mixture was added to diethyl ether (20 mL) and aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic phases were washed with water (30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 20% to 35% ethyl acetate in hexanes yielded **15** (1.361, 5.6 mmol, 66.0%) as a white solid. mp 105.0-106.2 °C; IR (film) 3339, 2835, 2738, 1686, 1603, 1573, 1389, 1209, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.88 (s, 2H), 7.78 (d, 4H, *J* = 8.2 Hz), 7.52 (d, 4H, *J* =

8.2 Hz), 5.93 (s, 1H), 3.77 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 149.7, 135.6, 130.0, 126.9, 75.1; high resolution mass spectrum (EI^+) calcd for $C_{15}H_{12}O_3$ (M^+) 240.0786, found 240.0793 *m/z*.



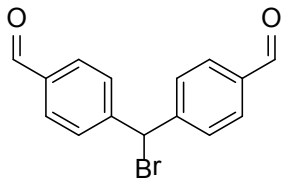
13

Silyl ether 13. A solution of benzhydrol **11** (11.11 g, 33.8 mmol, 1 eq.), *para*-toluenesulfonic acid (200 mg), and water (20 mL) in acetone (100 mL) was refluxed for 3 hours. After cooling, diethyl ether was added to effect the separation of layers. The aqueous was extracted with diethyl ether (3 x 20 mL). The combined organic phases were then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude alcohol was taken up in DMF (50 mL). Imidazole (6.91 g, 101.5 mmol, 3.0 eq.) and *tert*-butyldimethylsilyl chloride (7.65 g, 50.8 mmol, 1.5 eq.) were added and the mixture stirred at room temperature for 24 hours. Diethyl ether (50 mL) and water (50 mL) were added. The aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography using 20% diethyl ether in hexanes yielded **13** (7.523 g, 21.2 mmol, 62.7%) as a white crystalline solid. mp 84.8-86.0 °C; IR (film) 2954, 2929, 2857, 2734, 1702, 1604, 1578, 1471, 1254, 1208, 1086, 868,838, 793 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 2H), 7.82 (d, 4H, *J* = 8.2 Hz), 7.55 (d, 4H, *J* = 8.2 Hz), 5.88 (s, 1H), 0.92 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 150.7, 135.5, 129.9, 126.6, 76.0, 26.6, 18.1, -5.0; high resolution mass spectrum (EI^+) calcd for $C_{17}H_{17}O_3Si$ (M-$C_4H_9^+$) 297.0947, found 297.0945 *m/z*.



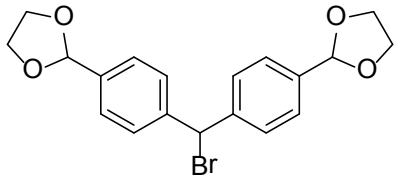
16

[Bis(4-[1,3]dioxolan-2-ylphenyl)methoxy]*tert*-butyldimethylsilane (16). To a solution of benzhydrol **11** (2.401 g, 7.3 mmol, 1.0 eq.) and imidazole (1.493 g, 22.0 mmol, 3 eq.) in DMF (7 mL) was added *tert*-butyldimethylsilyl chloride (1.653 g, 11.0 mmol, 1.5 eq.) at room temperature. After 24 hours, 20 mL of diethyl ether and 20 mL of water were added. The mixture was separated and the organic phase extracted with diethyl ether (3 x 20 mL). The combined organic phases were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography of the resulting yellow oil using 0% to 30% diethyl ether in hexanes yielded **16** (1.906 g, 4.3 mmol, 59.0%) as a white, crystalline solid. mp 98.7-101.0 °C; UV-Vis (CH_2Cl_2) λ_{max} (nm) 264 (ε = 61,057); IR (film) 2946, 2925, 2880, 2856, 1614, 1507, 1471, 1426, 1385, 1250, 1082, 1017, 870, 841, 776 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.41 (s, 8H), 5.84 (s 1H), 5.75 (s, 2H), 4.14-3.94 (m, 8H), 0.96 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 146.5, 137.4, 126.8, 126.5, 103.9, 76.6, 65.7, 26.0, 18.5, -4.8; high resolution mass spectrum (EI^+) calcd for $C_{21}H_{25}O_5Si$ ($M\text{-}C_4H_9^+$) 385.1471, found 385.1465 *m/z*.



18

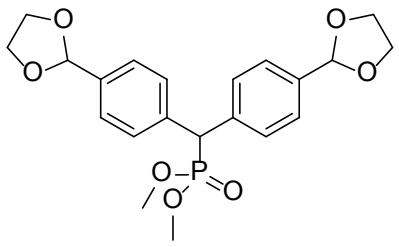
Bromide 18. To a solution of benzhydrol **11** (14.46 g, 44.0 mmol) in dichloromethane (250 mL) was added concentrated HBr (150 mL) and the mixture was refluxed until the alcohol was consumed as monitored by TLC. The reaction was cooled and the aqueous phased extracted with dichloromethane (2 x 40 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 20% to 40% ethyl acetate in hexanes yielded **18** (12.587 g, 41.5 mmol, 94.4%) as a yellow crystalline solid. mp 86.2-87.5 °C; IR (film) 3057, 2830, 2740, 1700, 1604, 1577, 1504, 1422, 1210, 800, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 2H), 7.85 (d, 4H, J = 8.2 Hz), 7.60 (d, 4H, J = 8.2 Hz), 6.31; ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 146.1, 136.0, 129.9, 129.0, 52.5; high resolution mass spectrum (EI^+) calcd for $C_{15}H_{10}{}^{79}BrO_2$ ($M\text{-}H^+$) 300.9864, found 300.9852 *m/z*.



17

Bromide 17. A solution of benzhydrol **11** (0.970 g, 2.95 mmol, 1 eq.) and triethylamine (1.24 mL, 0.90 g, 8.86 mmol, 3 eq.) in THF (5 mL) was cooled to 0 °C and stirred for 30 minutes. Methanesulfonyl chloride (0.25 mL, 0.372 g, 3.25 mmol, 1.1 eq.) was added, and the mixture was stirred an additional 30 minutes. The reaction was allowed to warm to room temperature

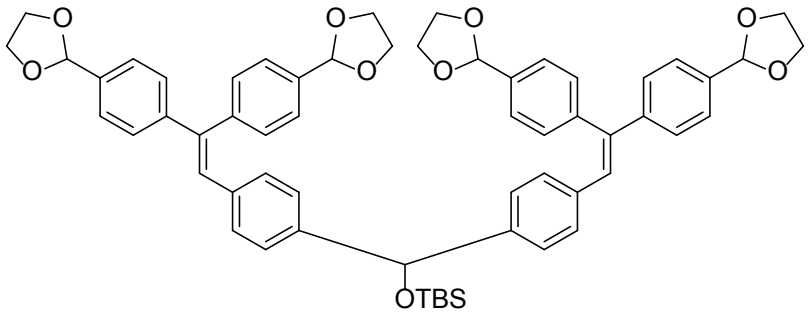
overnight. Lithium bromide (2.56 g, 30 mmol, 10 eq.) was added. After 1 hour, dichloromethane (15 mL) was added and the entire mixture then poured into saturated aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic phases were then washed with water (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography with 30% ethyl acetate in hexanes gave **17** (0.684 g, 1.75 mmol, 59.3%) as a light yellow solid. mp 65.0-66.8 °C; IR (film) 2955, 2887, 1614, 1511, 1473, 1427, 1391, 1301, 1221, 1082, 1020, 971, 943, 823, 788 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.50 (d, 4H, J = 8.6 Hz), 7.46 (d, 4H, J = 8.6 Hz), 6.35 (s, 1H), 5.78 (s, 2H), 4.11-3.98 (m, 8H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 142.2, 138.7, 128.7, 127.1, 103.5, 65.7, 54.9; high resolution mass spectrum (EI^+) calcd for $C_{19}H_{19}{}^{79}BrO_4$ (M^+) 390.0467, found 390.0470 *m/z*. Varying amounts of the analogous chloride were obtained in increasing amounts as the reaction was allowed to stir with lithium bromide for increasing amounts of time. The ^1H NMR of the chloride is indistinguishable but for the benzhydryl signal found at δ 6.14 ppm in the chloride. Low resolution mass spectrum (EI^+) supports the chloride product ($M\text{-}Cl^+$) *m/z* 311 with chlorine-containing fragments at 303/301 and 167/165.



11

[Bis(4-[1,3]dioxolan-2-ylphenyl)methyl]phosphonic acid dimethyl ester (11). The bromide **17** (3.190 g, 8.15 mmol, 1 eq.) was dissolved in toluene (50 mL) and trimethyl phosphite (1.92 mL, 2.02 g, 16.3 mmol, 2.0 eq.) was added and refluxed for 12 hours. Monitoring by TLC

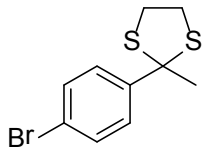
showed little progress, and so the solution was concentrated under reduced pressure. The residual oil was dissolved in 20 mL of phosphite and refluxed for 24 hours. After concentrating under reduced pressure, flash chromatography with 40% to 100% ethyl acetate in hexanes gave **11** (2.004 g, 4.8 mmol, 58.5%) as a white solid. mp 110.2-113.0 °C; IR (film) 2954, 2889, 1613, 1511, 1430, 1391, 1252, 1223, 1183, 1082, 1055, 1022, 972, 943, 898, 871, 823, 763 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54 (dd, 4H, J = 8.3 Hz, $^{4}J_{P\text{-}H}$ = 1.7 Hz), 7.44 (d, 4H, J = 8.3 Hz), 5.75 (s, 2H), 4.53 (d, 1H, $^{2}J_{P\text{-}H}$ = 24.9 Hz), 4.13-3.93 (m, 8H), 3.58 (d, 6H, $^{3}J_{P\text{-}H}$ = 10.7 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 137.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 137.7 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.6 (d, $J_{C\text{-}P}$ = 7.9 Hz), 127.1, 103.6, 65.6, 53.6 (d, $^{2}J_{C\text{-}P}$ = 7.3 Hz), 50.4 (d, $^{1}J_{C\text{-}P}$ = 137.5 Hz); ^{1}H NMR (300 MHz, Acetone-d6) δ 7.62 (dd, 4H, J = 8.2 Hz, $^{4}J_{P\text{-}H}$ = 1.8 Hz), 7.43 (d, 4H, J = 8.2 Hz), 5.71 (s, 2H), 4.73 (d, 1H, $^{2}J_{P\text{-}H}$ = 24.4 Hz), 4.07-3.92 (m, 8H), 3.53 (d, 6H, $^{3}J_{P\text{-}H}$ = 10.7 Hz); ^{13}C NMR (75 MHz, Acetone-d6) δ 139.1 (d, $J_{C\text{-}P}$ = 4.9 Hz), 138.5, 130.1 (d, $J_{C\text{-}P}$ = 7.9 Hz), 127.6, 104.0, 65.8, 53.4 (d, $^{2}J_{C\text{-}P}$ = 6.8 Hz), 50.2 (d, $^{1}J_{C\text{-}P}$ = 136.9 Hz); high resolution mass spectrum (EI^{+}) calcd for $C_{21}H_{24}O_7P$ ($M\text{-}H^{+}$) 419.1260, found 419.1255 *m/z*.



19

(Bis(4-[2,2-bis(4-[1,3]dioxolan-2-ylphenyl)vinyl]phenyl)methoxy)*tert*-butyldimethylsilane (19). To a solution of phosphonate **11** (0.502 g, 1.19 mmol, 2.05 eq) in THF (20 mL) cooled to 0 °C was added *n*-butyllithium (1.6 M in hexanes, 0.81 mL, 1.3 mmol, 2.2 eq.). After one hour,

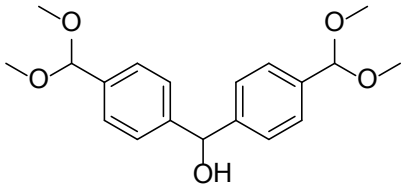
the dialdehyde **13** (0.204 g, 0.58 mmol, 1.0 eq.) in THF (5 mL) was added to the dark orange solution. The mixture was stirred overnight while warming to room temperature then quenched with water. The aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic phases were then washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 60% to 70% diethyl ether in hexanes as eluant gave **19** (0.230 g, 0.24 mmol, 42.1%) as a white solid. mp unsharp 72.8-109.5 °C; UV-Vis (CH_2Cl_2) λ_{max} 319 nm (ε = 37131), 236 nm (ε = 30482); IR (film) 2953, 2928, 2884, 2857, 1613, 1510, 1471, 1421, 1388, 1305, 1252, 1220, 1082, 1019, 970, 943, 868, 835, 776 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.46 (d, 4H, *J* = 8.1 Hz), 7.41 (d, 4H, *J* = 8.3 Hz), 7.32 (d, 4H, *J* = 8.3 Hz), 7.22 (d, 4H, *J* = 8.1 Hz), 7.14 (d, 4H, *J* = 8.2 Hz), 7.00 (s, 2H), 7.00 (d, 4H, *J* = 8.2 Hz), 5.81 (s, 2H), 5,78 (s, 2H), 5.63 (s, 1H), 4.15-4.00 (m, 16H), 0.90 (s, 9H), -0.04 (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 144.6, 144.3, 141.8, 141.6, 137.8, 136.3, 130.6, 129.8, 128.8, 127.8, 127.3, 126.7, 126.2, 103.9, 103.8, 76.5, 65.7, 65.6, 25.9, 18.5, -4.8; high resolution mass spectrum (ES^+) calcd for $C_{59}H_{62}O_9SiNa$ ($M+Na^+$) 965.4061, found 965.4152 *m/z*.



20

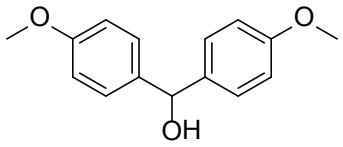
2-(4-Bromophenyl)-2-methyl-[1,3]dithiolane; compound with methane (20). To a solution of 4-bromoacetophenone (40.513 g, 203.5 mmol, 1.0 eq.) in toluene (250 mL) was added *para*-toluenesulfonic acid (0.595 g) and 1,2-ethanedithiol (90% purity, 19.5 mL, 21.8 g, 210 mmol, 1.05 eq.). The solution was refluxed in a Dean-Stark apparatus for 8 hours, cooled then added to water (100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under

reduced pressure. Flash chromatography with hexanes to remove residual thiol followed by 5% ethyl acetate in hexanes provided **20** (52.18 g, 189.6 mmol, 93.2%) as a clear liquid. IR (neat) 3057, 2964, 2921, 2859, 1584, 1486, 1392, 1275, 1077, 1007, 827, 732, 684 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 2H, J = 8.2 Hz), 7.43 (d, 2H, J = 8.2 Hz), 3.49-3.31 (m, 4H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 130.7, 128.5, 120.8, 67.8, 40.2, 33.3; high resolution mass spectrum (EI^+) calcd for $C_{10}H_{11}S_2{}^{79}Br$ (M^+) 273.9486, found 273.9474 *m/z*.



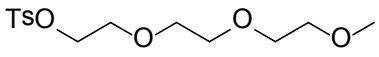
21

Bis(4-dimethoxymethylphenyl)methanol (21). To a solution of 4-bromobenzaldehyde dimethyl acetal (69.995 g, 302.9 mmol, 2.05 eq.) in THF (350 mL) cooled to -78 °C was added via cannula *n*-butyllithium in hexanes (2.5 M, 130 mL, 310 mmol, 2.1 eq.) over an hour. After an additional hour ethyl formate (12.0 mL, 11.004 g, 148.5 mmol, 1.0 eq.) in THF (100 mL) was added dropwise. The mixture was allowed to warm to room temperature overnight before it was quenched with water (150 mL) and stirred 45 minutes. The aqueous phase was extracted with diethyl ether (2 x 50 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography using 20% to 60% ethyl acetate in hexanes afforded **21** (47.05 g, 141.5 mmol, 95.3%) as a clear, viscous oil. IR (film) 3435, 2990, 2938, 2904, 2829, 1608, 1509, 1354, 1210, 1101, 1052, 817, 793 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.36 (m, 8H), 5.75 (s, 1H), 5.32 (s, 2H), 3.27 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 136.9, 126.5, 126.2, 102.8, 75.3, 52.4; high resolution mass spectrum (EI^+) calcd for $C_{19}H_{24}O_5$ (M^+) 332.1624, found 332.1612 *m/z*.



22

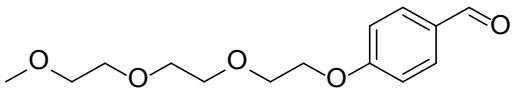
4,4'-Dimethoxybenzhydrol (22). To a solution of 4-bromoanisole (109.65 g, 586 mmol, 2.05 eq.) in THF (500 mL) cooled to -78 °C was added via cannula *n*-butyllithium in hexanes (1.6 M, 375 mL, 600 mmol, 2.1 eq.) over an hour. After 30 minutes ethyl formate (23.1 mL, 21.19 g, 286 mmol, 1.0 eq.) in THF (100 mL) was added dropwise. After 90 minutes water (200 mL) was added and the reaction warmed to room temperature. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. No further purification was necessary. On standing **22** (69.78 g, 285 mmol, 99.8%) crystallized as white needles. Clear prisms formed when recrystallized from a combination of petroleum ether and diethyl ether. mp 69.0-69.8 °C; IR (film) 3305, 3006, 2957, 2910, 2837, 1611, 1511, 1249, 1172, 1030, 812, 776 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, 4H, J = 8.6 Hz), 6.88 (d, 4H, J = 8.6 Hz), 5.72 (s, 1H), 3.79 (s, 6H), 2.79 (br s, 1H), in a dilute sample the benzhydryl and alcohol H appear at δ 5.79 (d, 1H, J = 3.4 Hz), 2.09 (d, 1H, J = 3.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 136.4, 127.6, 113.6, 75.1, 55.1; high resolution mass spectrum (EI^+) calcd for $C_{15}H_{16}O_3$ (M^+) 244.1099, found 244.1093 *m/z*.



36

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (36).[200] Sodium hydroxide (31.83 g, 796 mmol, 1.25 eq.) was dissolved in water (50 mL) and cooled to 0 °C. A solution of

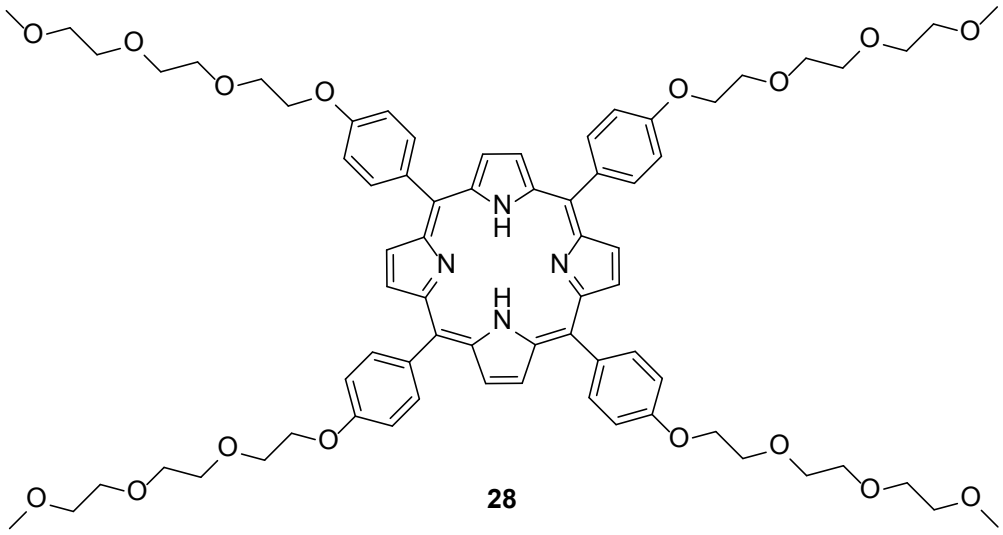
triethylene glycol monomethyl ether (104.52 g, 637 mmol, 1.0 eq.) in THF (50 mL) was added. Tosyl chloride (127.52 g, 669 mmol, 1.05 eq.) in THF (200 mL) was then added dropwise over the period of 60 minutes to the alcohol solution to maintain a temperature of 0 °C. Warmed to room temperature and stirred 36 hours. Addition tosyl chloride was added (15.00 g, 78.7 mmol, 0.12 eq.) and the solution stirred an additional 24 hours. With alcohol still present as monitored by TLC, sodium hydroxide (4.24 g, 106 mmol, 0.17 eq.) was added. The reaction was monitored and when all the alcohol was consumed, water (200 mL) was added and the reaction made acidic to litmus paper by addition of 6 M sulfuric acid. Dichloromethane (200 mL) was added and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 150 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (200 mL), water (200 mL), then brine (200 mL), dried over Na_2SO_4 and $MgSO_4$, filtered, and concentrated to yield **36** (198.37 g, 623 mmol, 97.8%) as a light, yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, 2H, J = 8.4 Hz), 7.15, (d, 2H, J = 8.4 Hz), 3.92-3.95 (m, 2H), 3.44-3.47 (m, 2H), 3.35-3.39 (m, 6H), 3.27-3.31 (m, 2H), 3.13 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 132.3, 129.2, 127.1, 71.1, 69.9, 69.7, 68.8, 67.9, 58.1, 20.8; high resolution mass spectrum (ES^+) calcd for ($M+H^+$) $C_{14}H_{23}O_6S$ 319.1215, found 319.1216 *m/z*.



27

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzaldehyde (27). 4-hydroxybenzaldehyde (5.129 g, 42.0 mmol, 1.0 eq.) and tosylate **36** (14.747 g, 46.3 mmol, 1.1 eq.) were dissolved in acetone (140 mL). Potassium carbonate (11.610 g, 84 mmol, 2.0 eq.) was added and the reaction refluxed for 24 hours during which a white precipitate formed. After cooling to room

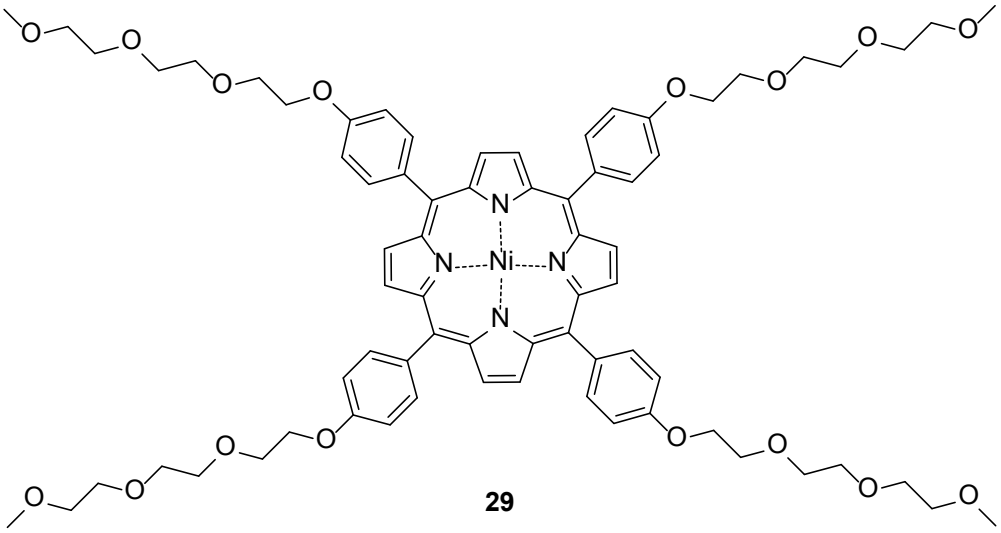
temperature, diethyl ether (100 mL) and water (75 mL) were added and the layers were separated. The aqueous phase was extracted with diethyl ether (2 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Flash chromatography using 50% to 75% ethyl acetate in hexanes gave **27** (9.880 g, 36.8 mmol, 87.7%) as a clear, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.69 (d, 2H, *J* = 9.0 Hz), 6.89 (d, 2H, *J* = 9.0 Hz), 4.07-4.10 (m, 2H), 3.74-3.77 (m, 2H), 3.59-3.61 (m, 2H), 3.50-3.57 (m, 4H), 3.39-3.41 (m, 2H), 3.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 163.4, 131.4, 129.6, 114.5, 71.4, 70.4, 70.2, 70.1, 69.0, 67.4, 58.5; high resolution mass spectrum (ES^+) calcd for ($M-H^+$) $C_{14}H_{19}O_5$ 267.1232, found 267.1233 *m/z*.



28

5,10,15,20-Tetra(4-OMTEG-phenyl)porphyrin (28). Aldehyde **27** (4.166 g, 15.5 mmol, 1.0 eq.) and pyrrole (1.07 mL, 1.04 g, 15.5 mmol, 1.0 eq.) were dissolved in chloroform (1.5 L) and purged with nitrogen for 15 minutes. $BF_3{\cdot}OEt_2$ (0.19 mL, 0.21 g, 1.5 mmol, 0.1 eq.) was added and the reaction stirred for 150 minutes. DDQ (2.64 g, 11.6 mmol, 0.75 eq.) was added and the solution went from dark red to black. After 60 minutes, triethylamine (2.16 mL, 1.59 g, 15.5 mmol, 1.0 eq.) was added. The solution was concentrated and combined with the products of

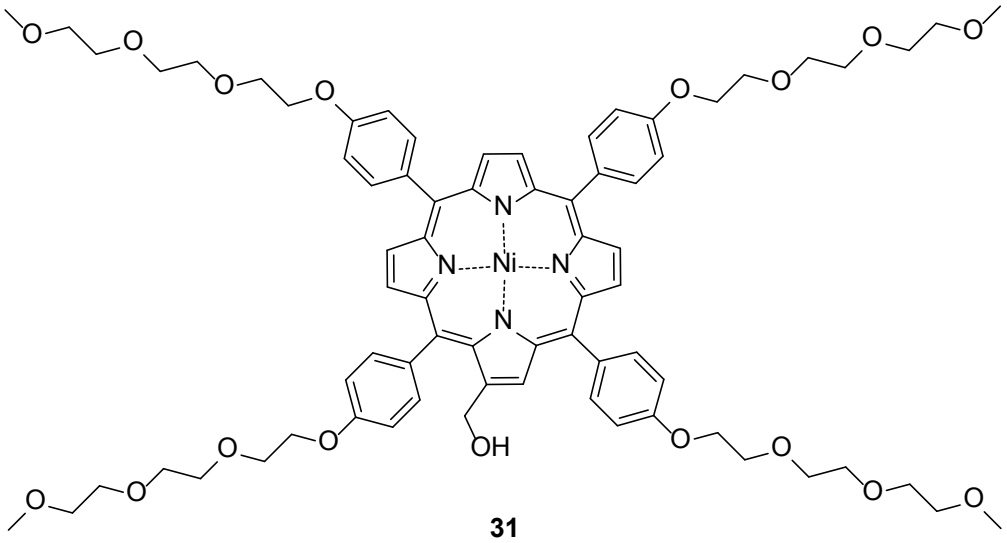
three similar preparations. The combined crude mixture was loaded onto ~50 g of silica gel. Flash chromatography using 60:40 chloroform:ether followed by 2:68:30 then 5:65:30 methanol:chloroform:ether yielded **28** (6.637 g, 5.3 mmol, 33.8%) as a shiny, purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 8H), 8.12 (d, 8H, *J* = 8.4 Hz), 7.30 (d, 8H, *J* = 8.4 Hz), 4.41-4.47 (m, 8H), 4.05-4.08 (m, 8H), 3.87-3.91 (m, 8H), 3.79-3.83 (m, 8H), 3.74-3.77 (m, 8H), 3.62-3.65 (m, 8H), 3.44 (s, 12H), -2.74 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 135.5, 134.8, 131.0, 119.7, 112.9, 72.0, 71.0, 70.8, 70.7, 69.9, 67.7, 59.1.



29

Ni-porphyrin (29). Free base porphyrin **28** (6.632 g, 5.2 mmol, 1.0 eq) and nickel(II) acetate tetrahydrate (6.531 g, 26.2 mmol, 5.0 eq.) were dissolved in chloroform (150 mL) and methanol (75 mL). After refluxing for 24 hours, the solution was cooled to room temperature and stirred an additional 72 hours. The solution was condensed and the mixture loaded onto silica. Flash chromatography with 2:70:30 methanol:chloroform:ether followed by 3:70:30 and 6:70:30 of the same solvent system yielded **29** (6.265 g, 4.7 mmol, 90.4%) as a red-purple solid. UV-vis (CH_2Cl_2) λ_{max} 529 (ε = 22,500) 418 (ε = 262,581); IR (film) 2923, 2880, 1608, 1507, 1454, 1353, 1282, 1249, 1177, 1134, 1108, 1062, 1000, 806 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.84 (s,

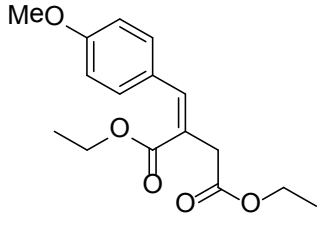
8H), 7.93 (d, 8H, J = 8.4 Hz), 7.18 (d, 8H, J = 9.0 Hz), 4.20-4.23 (m, 8H), 3.85-3.88 (m, 8H), 3.70-3.73 (m, 8H), 3.62-3.67 (m, 16H), 3.54-3.57 (m, 8H), 3.40 (s, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.0, 143.5, 135.1, 133.7, 132.4, 119.3, 113.3, 72.3, 71.1, 70.9, 70.8, 70.0, 68.0, 59.0; high resolution mass spectrum (ES^+) calcd for ($M+H^+$) $C_{72}H_{85}N_4O_{16}Ni$ 1319.5314, found 1319.5394 *m/z*; Anal. Calcd for $C_{72}H_{84}N_4O_{16}Ni$: C, 65.51; H, 6.41; N, 4.24; Ni, 4.45. Found: C, 65.47; H, 6.49; N, 4.26; Ni, 4.24.



31

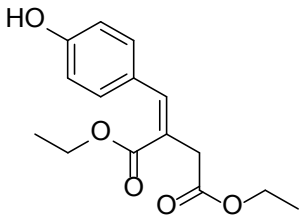
Ni-Porphyin alcohol (31). Ni-porphyrin **29** (1.2107 g, 0.92 mmol, 1.0 eq.) was dissolved in chloroform (30 mL). DMF (5.11 mL, 4.83 g, 66 mmol, 72 eq.) was cooled to 0 °C. $POCl_3$ (5.13 mL, 8.44 g, 55 mmol, 60 eq.) was added slowly via syringe. After stirring 3 minutes at 0 °C, the flask was removed from the ice bath and the mixture stirred an additional 5 minutes. Chloroform (3 mL) was then added to the viscous, dark red liquid to aid in transfer. The Vilsmeier reagent was added to the porphyrin solution via syringe and the mixture was refluxed for 2.5 hours with a drying tube attached to the top of the condenser. The reaction mixture was then cooled in an ice bath and quenched very slowly with saturated aqueous $NaHCO_3$. The mixture was stirred

vigorously for 30 minutes and warmed to room temperature during which time to color changed from green to a dark brown/purple color. The layers were separated and extracted with ethyl acetate (3 x 25 mL). The combined organic phases were washed with water (100 mL) and dried over Na_2SO_4, filtered and concentrated to yield crude Ni-porphyrin aldehyde **30**. This was dissolved in THF (50 mL) and cooled to 0 °C. Sodium borohydride (0.1392 g, 3.68 mmol, 4.0 eq) was added carefully and the reaction allowed to warm to room temperature slowly. After 3.5 hours, the reaction was complete and so it was cooled again to 0 °C and quenched with water (50 mL) and then extracted with ethyl acetate (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. Flash chromatography of the crude solid loaded onto silica with 0:50:50, 3:50:50, then 6:50:50 methanol:ether:chloroform yielded **31** (1.1100 g, 0.82 mmol, 89.4%) as a dark purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.70-8.77 (m, 6H), 7.87-7.91 (m, 6H). 7.76 (d, 2H, J = 8.4 Hz), 7.16-7.22 (m, 8H), 4.81 (s, 2H), 4.33-4.36 (m, 8H), 3.99 (m, 8H), 3.83-3.85 (m, 8H), 3.71-3.29 (m, 16H), 3.61-3.63 (m, 8H), 3.42-3.43 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 158.5, 147.1, 143.6, 142.9, 142.9, 142.7, 142.5, 142.4, 141.3, 139.0, 134.6, 133.4, 133.3, 133.2, 133.1, 132.0, 118.9, 118.5, 117.5, 117.4, 113.5, 113.0, 71.9, 70.9, 70.7, 70.6, 69.8, 67.6, 61.4, 59.0; high resolution mass spectrum (ES^+) calcd for ($M+Na^+$) $C_{73}H_{86}N_4O_{17}NaNi$ 1371.5239, found 1371.5239 *m/z*.



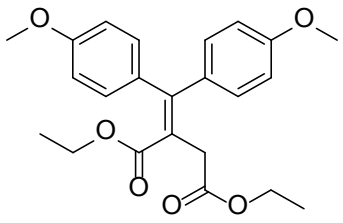
37

Diethyl 2-(4-methoxybenzylidene)succinate (37). 4-methoxybenzaldehyde (6.085 g, 44.7 mmol, 1.0 eq.) and diethyl succinate (10.41 mL, 10.90 g, 62.6 mmol, 1.4 eq.) were dissolved in THF (60 mL) and added dropwise to a solution of potassium *tert*-butoxide (7.025 g, 62.6 mmol, 1.4 eq.) in THF (50 mL) over a period of two hours. The reaction was heated to reflux for 16 hours then cooled to room temperature. Water (50 mL) and diethyl ether (50 mL) were added and the layers separated. The organic phase was extracted with 2 M aqueous NaOH (2 x 50 mL). The combined aqueous layers were acidified with 6 M aqueous HCl to pH 1 (approximately 40 mL) and extracted with dichloromethane (3 x 25 mL). The dichloromethane phase was then dried over Na_2SO_4 and $MgSO_4$, filtered, and concentrated. The crude monoester was dissolved in ethanol (75 mL) and 10 drops of concentrated H_2SO_4 were added. The solution was refluxed for 16 hours and cooled to room temperature. Dichloromethane (50 mL) and water (50 mL) were added, and the layers were separated. The aqueous phase was extracted with dichloromethane (2 x 50 mL). The combined organic phases were washed with brine (50 mL). Diethyl ether (25 mL) was added to remove additional water dissolved in the organic phase due to remaining alcohol. The organic phases were dried over $MgSO_4$, filtered and concentrated to yield **37** (5.626 g, 19.2 mmol, 43.1%) as a bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.33 (d, 2H, J = 9.0 Hz), 6.91 (d, 2H, J = 9.0 Hz), 4.24 (q, 2H, J = 7.2 Hz), 4.19 (q, 2H, J = 7.2 Hz), 3.82 (s, 3H), 3.55 (s, 2H), 1.32 (t, 3H, J = 7.2 Hz), 1.26 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 167.5, 160.1, 141.3, 130.8, 127.4, 124.2, 114.0, 60.9, 60.8, 55.2, 33.7, 14.2, 14.1; high resolution mass spectrum (ES^+) calcd for ($M+Na^+$) $C_{16}H_{20}O_5Na$ 315.1208, found 315.1206 *m/z*.



38

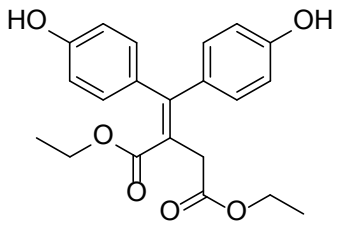
Diethyl 2-(4-hydroxybenzylidene)succinate (38). Boron tribromide (1M in dichloromethane, 9.7 mL, 9.7 mmol, 2.0 eq.) was added to a solution of methyl ether **37** (1.4140 g, 4.84 mmol, 1.0 eq.) in dichloromethane (30 mL) that had been cooled to 0 °C. After stirring for one hour, the solution was warmed to room temperature and stirred an additional two hours. Ethanol (4 mL) was added to quench the reaction. After pouring into ice cold water (50 mL) the layers were separated, and the aqueous phase was extracted with dichloromethane (25 mL) then ethyl acetate (25 mL). The combined organic phases were washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated. The crude phenol was dissolved in ethanol (100 mL) to which ~1 mL concentrated H_2SO_4 was added. The solution was refluxed for 18 hours, cooled and concentrated by half its original volume. Ethyl acetate (50 mL) was added followed by saturated aqueous $NaHCO_3$ (50 mL), and the layers were separated. The aqueous phase was extracted with ethyl acetate (2 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, filtered, concentrated and loaded onto silica. Flash chromatography with 5% methanol in chloroform yielded **38** (447.7 mg, 1.61 mmol, 33.2%) as a bright orange solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.78 (s, 1H), 7.77 (s, 1H), 7.34 (d, 2H, J = 8.7 Hz), 6.91 (d, 2H, J = 8.7 Hz), 4.21 (q, 2H, J = 7.2 Hz), 4.14 (q, 2H, J = 7.2 Hz), 3.54 (s, 2H), 1.31 (t, 3H, J = 7.2 Hz), 1.23 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, Acetone-d6) δ 171.5, 168.0, 141.8, 132.1, 127.3, 124.9, 116.5, 61.3, 61.2, 34.3, 14.6, 14.5; high resolution mass spectrum (ES^+) calcd for ($M+Na^+$) $C_{15}H_{18}O_5Na$ 301.1052, found 301.1044 *m/z*.



24

Diethyl 2-(bis(4-methoxyphenyl)methylene)succinate (24). 4,4'-dimethoxybenzophenone **7** (14.333 g, 59.2 mmol, 1.0 eq.) and diethyl succinate (11.81 mL, 12.36 g, 71.0 mmol, 1.2 eq.) were dissolved in THF (30 mL). Potassium *tert*-butoxide (7.969 g, 71.0 mmol, 1.2 eq.) in THF (100 mL) was added dropwise. The reaction was heated to reflux for 16 hours then cooled to room temperature. Water (50 mL) and diethyl ether (100 mL) were added and the layers separated. The organic phase was extracted with 2 M aqueous NaOH (2 x 50 mL). The combined aqueous layers were acidified with 6 M aqueous HCl to pH 1 (approximately 30 mL) and extracted with dichloromethane (2 x 50 mL). The dichloromethane phase was then dried over $MgSO_4$, filtered, and concentrated. The crude monoester was dissolved in ethanol (125 mL) to which ~1 mL concentrated H_2SO_4 was added. The solution was refluxed for 44 hours, cooled and concentrated by half its original volume. Ethyl acetate (100 mL) was added followed by water (50 mL), and the layers were separated. The aqueous phased was extracted with ethyl acetate (30 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (100 mL). That aqueous phase was extracted with ethyl acetate (20 mL). The combined organic phases were dried over $MgSO_4$, filtered, concentrated, and loaded onto silica. Flash chromatography with 50 % diethyl ether in hexanes yielded **24** (18.400 g, 46.2 mmol, 78.0%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, 2H, J = 9.0 Hz), 7.04 (d, 2H, J = 8.7 Hz), 6.85 (d, 2H, J = 8.7 Hz), 6.80 (d, 2H, J = 8.7 Hz), 4.17 (q, 2H, J = 7.2 Hz), 3.98 (q, 2H, J = 7.2

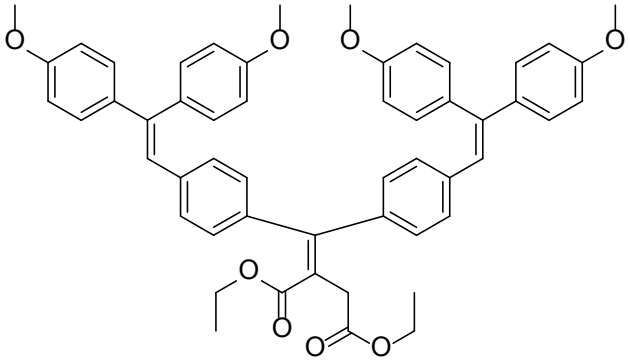
Hz), 3.80 (s, 3H), 3.79 (s, 3H), 3.47 (s, 2H), 1.26 (t, 3H, J = 7.2 Hz), 0.94 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 169.9, 159.5, 159.4, 151.0, 134.8, 133.2, 130.8, 123.4, 113.5, 113.1, 60.7, 60.4, 55.2, 38.6, 14.1, 13.6; high resolution mass spectrum (ES^+) calcd for ($M+H^+$) $C_{23}H_{27}O_6$ 399.1808, found 399.1803 *m/z*.



26

Diethyl 2-(bis(4-hydroxyphenyl)methylene)succinate (26). Boron tribromide (1M in dichloromethane, 20.0 mL, 20.0 mmol, 4.0 eq.) was added to a solution of methyl ether **26** (2.033 g, 5.1 mmol, 1.0 eq.) in dichloromethane (30 mL) that had been cooled to -78 °C. After stirring for 3.5 hours, additional boron tribromide (5.0 mL, 5.0 mmol, 0.25 eq.) was added, the solution was warmed to room temperature and stirred an additional 90 minutes. Ethanol (15 mL) was added to quench the reaction. After pouring into water (50 mL) the layers were separated, and the aqueous phase was extracted with ethyl acetate (2 x 30 mL). The combined organic phases were washed with brine (25 mL), dried over $MgSO_4$, filtered and concentrated. The crude phenol **25** was dissolved in ethanol (75 mL) to which ~0.5 mL concentrated H_2SO_4 was added. The solution was refluxed for 16 hours, cooled and concentrated by half its original volume. Ethyl acetate (50 mL) was added and the solution was washed with water (50 mL) followed by saturated aqueous $NaHCO_3$ (50 mL). The aqueous phase was extracted with ethyl acetate (2 x 25 mL). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$, filtered, concentrated, and loaded onto silica. Flash chromatography with a gradient of

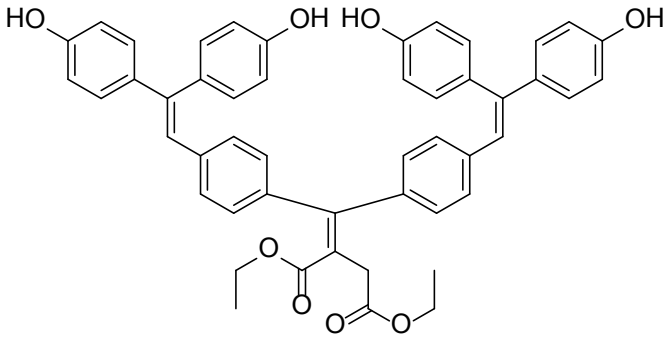
33% to 50% ethyl acetate in hexanes yielded **26** (1.2901 g, 3.5 mmol, 68.3%) as an off white solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.57 (s, 1H), 8.43 (s, 1H), 6.98 (d, 2H, *J* = 8.7 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 6.83 (d, 2H, *J* = 8.4 Hz), 6.76 (d, 2H, *J* = 8.7 Hz), 4.11 (q, 2H, *J* = 7.2 Hz), 3.89 (q, 2H, *J* = 7.2 Hz), 3.39 (s, 2H), 1.21 (t, 3H, *J* = 7.2 Hz), 0.90 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, Acetone-d6) δ 171.7, 170.3, 158.4, 158.3, 151.9, 134.9, 133.3, 131.7, 131.3, 123.9, 115.9, 115.4, 61.0, 60.6, 39.2, 14.5, 14.0; high resolution mass spectrum (ES^{+}) calcd for (M+Na^{+}) $C_{21}H_{22}O_6Na$ 393.1314, found 393.1307 *m/z*.



39

Diethyl 2-(bis(4-(2,2-bis(4-methoxyphenyl)vinyl)phenyl)methylene)succinate (39). G1-Ketone **9** (1.0487 g, 1.6 mmol, 1.0 eq.) and diethyl succinate (0.80 mL, 0.83 g, 4.8 mmol, 3.0 eq.) were dissolved in THF (75 mL). Potassium *tert*-butoxide (0.5502 g, 4.8 mmol, 3.0 eq.) in THF (100 mL) was added dropwise. The reaction was heated to reflux for 20 hours then cooled to room temperature. Water (25 mL) and diethyl ether (25 mL) were added and the layers separated. The organic phase was extracted with 2 M aqueous NaOH (2 x 25 mL). The combined aqueous layers were acidified with 10% aqueous HCl to pH 1 and extracted with dichloromethane (3 x 25 mL) then ethyl acetate (25 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated. The crude monoester was dissolved in 1,2-dichloroethane

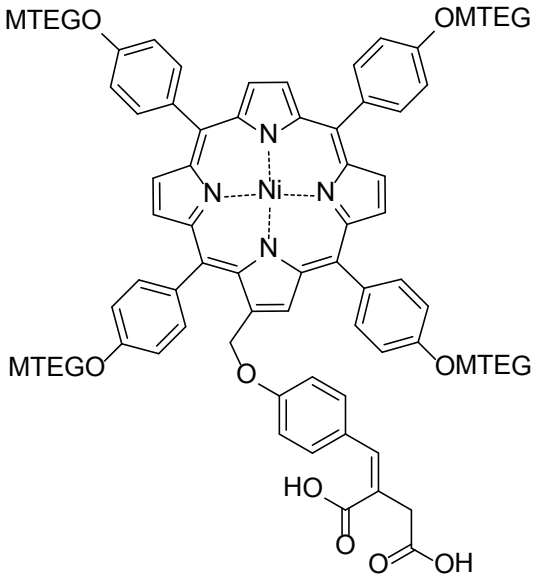
(25 mL). Ethanol (50 mL) and ~0.5 mL concentrated H_2SO_4 were added. The solution was refluxed for 20 hours, cooled and concentrated by half its original volume. Ethyl acetate (50 mL) was added followed by water (25 mL), and the layers were separated. The organic phases were washed with water (25 mL) then saturated aqueous $NaHCO_3$ (25 mL). That aqueous phase was extracted with ethyl acetate (25 mL). The combined organic phases were dried over $MgSO_4$, filtered, concentrated, and loaded onto silica. Flash chromatography with a gradient from 20% to 40% to 50 % diethyl ether in hexanes removed the most polar impurities. After loading onto silica, a second column with 20%, 30%, then 40% diethyl ether in hexanes yielded **39** (498.0 mg, 0.61 mmol, 38.2%) as a yellow solid. IR (film) 3034, 2956, 2934, 2905, 2836, 1734, 1702, 1603, 1572, 1511, 1463, 1442, 1419, 1389, 1368, 1325, 1286, 1247, 1175, 1111, 1033, 835, 780, 737, 703 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.27 (d, 4H, J = 8.7 Hz), 7.12 (d, 2H, J = 8.4 Hz), 7.12 (d, 2H, J = 8.7 Hz), 7.02 (d, 2H, J = 8.1 Hz), 6.93 (d, 2H, J = 8.4 Hz), 6.85-6.90 (m, 14H), 4.14 (q, 2H, J = 7.2 Hz), 3.94 (q, 2H, J = 7.2 Hz), 3.84 (s, 3H), 3.83 (s, 3H), 3.81 (s, 6H), 3.40 (s, 2H), 1.25 (t, 3H, J = 7.2 Hz), 0.96 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 171.5, 169.7, 159.9, 159.8, 159.6, 159.6, 151.2, 143.1, 142.6, 140.5, 138.8, 138.5, 138.0, 136.5, 136.5, 133.0, 132.9, 131.8, 129.5, 129.3, 129.2, 129.2, 129.1, 128.9, 125.9, 125.7, 125.3, 114.4, 113.9, 61.2, 60.9, 55.5, 55.5, 38.7, 14.3, 13.9; high resolution mass spectrum (ES^+) calcd for ($M+Na^+$) $C_{53}H_{50}O_8Na$ 837.3403, found 837.3383 *m/z*.



40

Diethyl 2-(bis(4-(2,2-bis(4-hydroxyphenyl)vinyl)phenyl)methylene)succinate (40). Boron tribromide (1M in dichloromethane, 6.0 mL, 6.0 mmol, 10.0 eq.) was added in three portions at ten minute intervals in a rapid dropwise fashion to a solution of methyl ether **39** (0.4854 g, 0.60 mmol, 1.0 eq.) in dichloromethane (10 mL) that had been cooled to -78 °C. After stirring for four hours, additional boron tribromide (3.0 mL, 3.0 mmol, 5.0 eq.) was added, the solution was warmed to room temperature and stirred an additional 60 minutes. The reaction was quenched by cooling to -78 °C and the addition of ethanol (5 mL). After pouring into water (25 mL) the layers were separated, and the aqueous phase was extracted with ethyl acetate (2 x 20 mL). The combined organic phases were washed with brine (25 mL), dried over $MgSO_4$, filtered and concentrated. The crude phenol was dissolved in ethanol (30 mL) to which ~0.2 mL concentrated H_2SO_4 was added. The solution was refluxed for 16 hours, cooled and concentrated by half its original volume. Ethyl acetate (50 mL) was added followed by water (25 mL), and the layers were separated. The aqueous phase was extracted with ethyl acetate (2 x 20 mL). The combined organic phases were washed with brine (25 mL), dried over $MgSO_4$, filtered, concentrated, and loaded onto silica. Flash chromatography with 50% ethyl acetate in hexanes yielded **40** (0.3830 g, 0.50 mmol, 84.1%) as an orange solid. IR (film) 3386, 2978, 2876, 1705, 1608, 1512, 1441, 1370, 1327, 1267, 1171, 1102, 1024, 838 cm^{-1}; ^1H NMR (300 MHz, Acetone-d6) δ 8.44 (s, 4H) 7.16-7.20 (m, 4H), 7.04 (d, 2H, *J* = 8.1 Hz), 6.96-7.00 (m, 6H), 6.88 (d, 2H, *J*

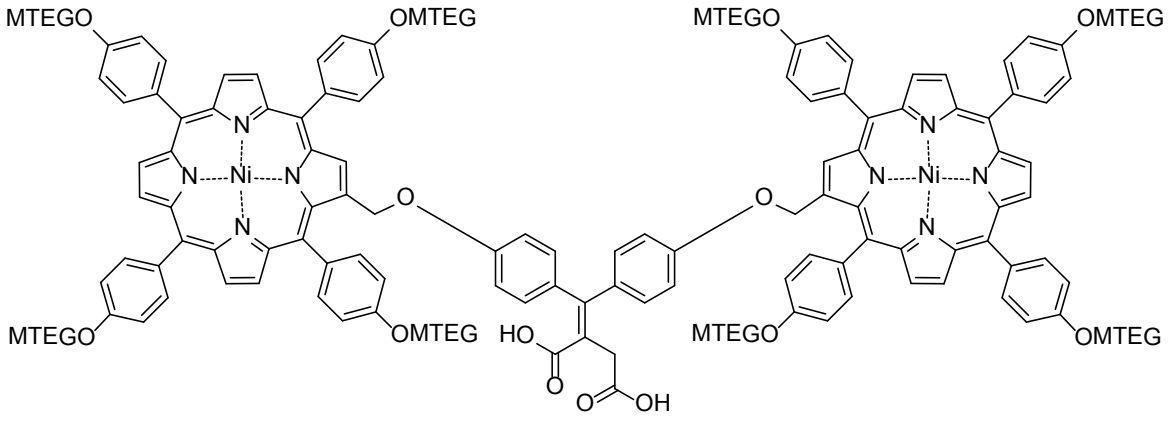
= 8.4 Hz), 6.78-6.85 (m, 12H), 4.09 (q, 2H, *J* = 6.9 Hz), 3.87 (q, 2H, *J* = 7.2 Hz), 3.33 (s, 2H), 1.21 (t, 3H, *J* = 6.9 Hz), 0.90 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, Acetone-d6) δ 171.3, 169.7, 158.2, 158.1, 157.9, 157.8, 151.3, 144.1, 143.6, 140.93, 139.2, 139.2, 138.6, 135.9, 135.8, 132.4, 132.3, 132.2, 132.1, 129.9, 129.7, 129.6, 129.6, 129.2, 125.9, 125.4, 125.1, 116.5, 116.4, 115.9, 61.2, 60.9, 38.8, 14.5, 14.0; high resolution mass spectrum (ES^-) calcd for ($M-H^+$) $C_{49}H_{41}O_8$ 757.2801, found 757.2722 *m/z*.



33

1P-Dye (33). Ni-Porphyrin alcohol **31** (0.6350 g, 0.49 mmol, 1.3 eq.), phenol **38** (0.1083 g, 0.39 mmol, 1.0 eq.) and triphenylphosphine (0.1233 g, 0.47 mmol, 1.2 eq.) were dissolved in THF (8 mL) and cooled to 0 °C. DIAD (0.09 mL, 0.09 g, 0.47 mmol, 1.2 eq.) was added dropwise and the solution was stirred 10 minutes at 0 °C then warmed to room temperature. The reaction was monitored by TLC, and after 24 hours was not complete. The reaction was cooled to 0 °C, and a second portion of triphenylphosphine and DIAD equal to the first were added. Once the reaction was complete, the solution was concentrated. Flash chromatography with 2.5% methanol in

chloroform yielded a set of fractions with the product and triphenylphosphine. The mixture was adsorbed to silica and subjected to flash chromatography with 60% ethyl acetate in hexanes followed by 3% methanol in chloroform yielded the mostly pure succinate diester. This was dissolved in THF (20 mL) and a 1 M aqueous sodium hydroxide (10 mL) was added. The mixture was refluxed for 48 hours. An additional 10 mL of aqueous sodium hydroxide was added, and the solution was refluxed three hours longer. After cooling to room temperature, 10% HCl (20 mL) was added followed by chloroform (20 mL). The layers were separated. The aqueous phase was extracted with chloroform (2 x 20 mL). The combined organic phases were concentrated onto silica. Flash chromatography with 5% to 10% methanol in chloroform yielded **33** (0.1480 g, 0.09 mmol, 23.2%) as a purple solid. UV-vis (CH_2Cl_2) λ_{max} 532 (ε = 29,034), 420 (ε = 294,754); IR (film) 3445, 3034, 2877, 1704, 1637, 1606, 1573, 1507, 1453, 1409, 1352, 1284, 1248, 1199, 1177, 1109, 1030, 1005, 945, 849, 815, 720 cm^{-1}; high resolution mass spectrum (ES^-) calcd for ($M-H^+$) $C_{84}H_{93}N_4O_{21}Ni$ 1551.5686, found 1551.5592 *m/z*.

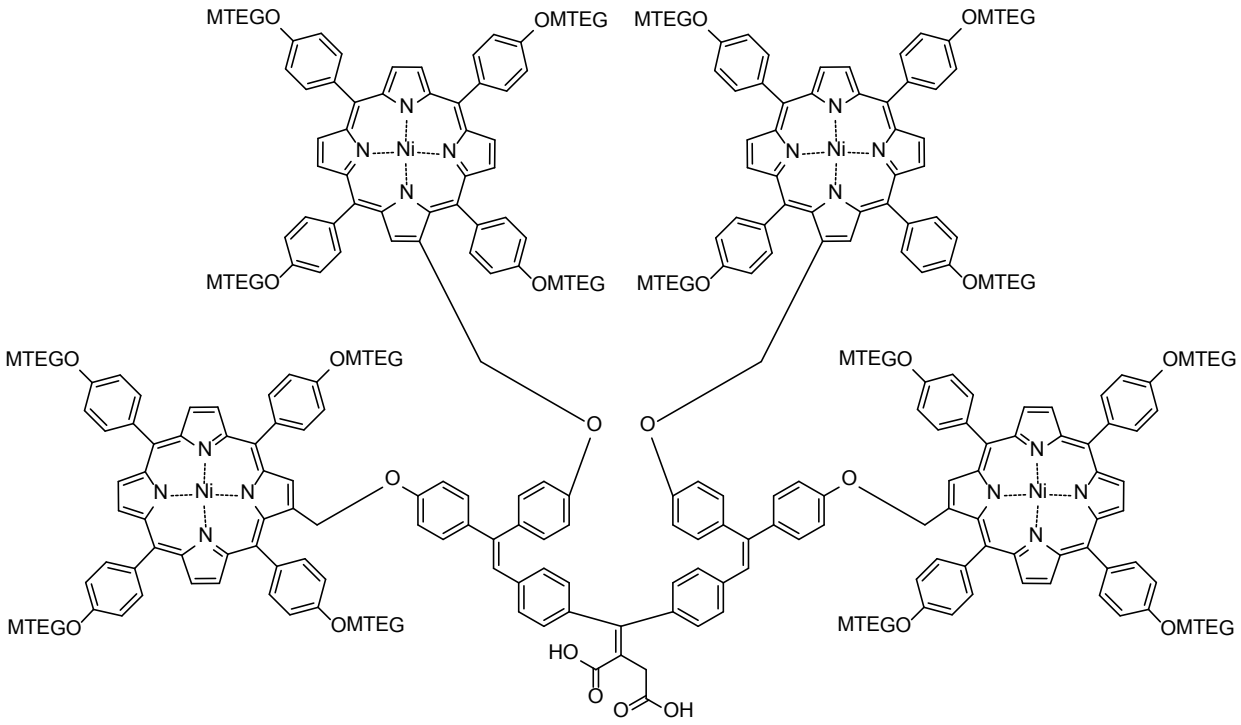


34

2P-Dye (34). Ni-Porphyrin alcohol **31** (0.7358 g, 0.54 mmol, 2.3 eq.), phenol **26** (0.0878 g, 0.24 mmol, 1.0 eq.) and triphenylphosphine (0.1367 g, 0.52 mmol, 2.2 eq.) were dissolved in THF (8 mL) and cooled to 0 °C. DIAD (0.10 mL, 0.11 g, 0.52 mmol, 2.2 eq.) was added dropwise and

the solution was warmed to room temperature over three hours. The reaction was monitored by TLC, and after 72 hours was not complete. The reaction was cooled to 0 °C, and a second portion of triphenylphosphine and DIAD equal to the first were added. After 44 hours, the solution was concentrated and adsorbed to silica. Flash chromatography with 2.5% methanol in chloroform yielded a set of fractions with the product and triphenylphosphine. The mixture was adsorbed to silica and subjected to flash chromatography with 60/30/10, 50/40/10, then 25/70/6 diethyl ether/chloroform/methanol which elutes unreacted porphyrin first followed by the product succinate diester (403 mg). This was dissolved in THF (20 mL) and a 1 M aqueous sodium hydroxide (10 mL) was added. The mixture was refluxed for 20 hours. An additional 10 mL of 2 M aqueous sodium hydroxide was added, and the solution was refluxed 18 hours longer. The two layers present were separated. The aqueous phase was acidified with 1 M aqueous HCl and extracted with ethyl acetate (2 x 30 mL). After concentrating the combined organic phases, the crude was dissolved in THF (30 mL). Water (6 mL) and 2 M aqueous sodium hydroxide (2 mL) was added and the mixture refluxed 20 hours. A solution of THF (4 mL), water (4 mL), and 2 M aqueous sodium hydroxide (1.5 mL) was added to the reaction, and it was refluxed an additional 18 hours at which point it was complete. After cooling, ethyl acetate (30 mL) was added followed by 1 M HCl (30 mL) and the layers were separated. The red aqueous layer was extracted with chloroform (2 x 30 mL) until it became clear and colorless. The combined organic phases were dried over Na_2SO_4, filtered, concentrated, and adsorbed to silica. Flash chromatography with a series of methanol/diethyl ether/chloroform mixtures: 5/35/60, 7/33/60, 10/30/60, 13/17/70, and 1/1/4. The diacid **34** (0.1949 g, 0.07 mmol, 27.2%) was a shiny purple solid. UV-vis (CH_2Cl_2) λ_{max} 532 (ε = 47,435), 420 (ε = 519,727); IR (film) 3447, 3035, 2876, 1729, 1698, 1607, 1573, 1507, 1453, 1411, 1352, 1328, 1284, 1248, 1199, 1177, 1110, 1064,

1030, 1005, 943, 850, 816, 800, 720, 646 cm^{-1}; Anal. Calcd for $C_{163}H_{182}N_8O_{38}Ni_2$: C, 65.73; H, 6.16; N, 3.76; Ni, 3.94. Found: C, 64.72; H, 6.18; N, 3.65; Ni, 3.68.



35

4P-Dye (35). Ni-Porphyrin alcohol **31** (1.1089 g, 0.82 mmol, 4.3 eq.), phenol **40** (0.1449 g, 0.19 mmol, 1.0 eq.) and triphenylphosphine (0.2154 g, 0.82 mmol, 4.3 eq.) were dissolved in THF (20 mL) and cooled to 0 °C. DIAD (0.16 mL, 0.17 g, 0.82 mmol, 4.3 eq.) was added dropwise and the solution was stirred 10 minutes at 0 °C then warmed to room temperature for 18 hours. The reaction was heated to reflux for 24 hours. A second portion of triphenylphosphine and DIAD was added equal to the first. The solution was refluxed for 18 hours, cooled to room temperature, concentrated and adsorbed to silica. Flash chromatography with a series of methanol/diethyl ether/chloroform mixtures: 0/70/30, 5/75/20, 5/70/25, 10/60/30, and 5/30/65 elutes the unreacted porphyrin first followed by the product diester (1.04 g), a dark purple solid.

This was dissolved in THF (30 mL) and a 0.5 M aqueous sodium hydroxide (4 mL) was added. The mixture was refluxed for 14 hours. An additional 20 mL of 0.5 M aqueous sodium hydroxide was added, and the solution was refluxed for 20 hours. After cooling to room temperature, 10% HCl (25 mL) was added followed by dichloromethane (50 mL). The layers were separated. The aqueous phase was extracted with dichloromethane (2 x 25 mL). The combined organic phases were washed with brine (50 mL), then water (50 mL) with 10% HCl (25 mL) added. The partially reacted mixture was concentrated, then redissolved in THF (30 mL) along with 2 M aqueous sodium hydroxide (10 mL) and methanol (10 mL). After refluxing 18 hours, the solution was cooled before being quenched with 1 M HCl (25 mL). Dichloromethane (25 mL) was added and the layers separated. The aqueous phase was extracted with dichloromethane (2 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and loaded onto silica. Flash chromatography with a series of methanol/diethyl ether/chloroform mixtures: 5/60/35, 10/60/30, and 5/0/95 yielded **35** (0.5925 g, 0.09 mmol, 51.7%) as a dark purple solid. UV-vis (CH_2Cl_2) λ_{max} 533 (ε = 75,714), 421 (ε = 888,772), 333 (ε = 110,506); IR (film) 3457, 3034, 2875, 1702, 1607, 1507, 1411, 1352, 1283, 1248, 1199, 1177, 1110, 1064, 1031, 1005, 928, 816, 719 cm^{-1}; Anal. Calcd for $C_{337}H_{370}N_{16}O_{72}Ni_4$: C, 67.11; H, 6.18; N, 3.72; Ni, 3.89. Found: C, 66.60; H, 6.11; N, 3.59; Ni, 3.76.

APPENDIX A

^{1}H AND ^{13}C NMR DATA

NMR data is included in the order the compounds are presented in the experimentals. The ^{1}H spectrum is included first in all cases. In instances where multiple spectra were collected using different solvents, the solvent is indicated to the lower right of the structure.

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integral

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80
100
120
140
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200
ppm

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Integral
ppm

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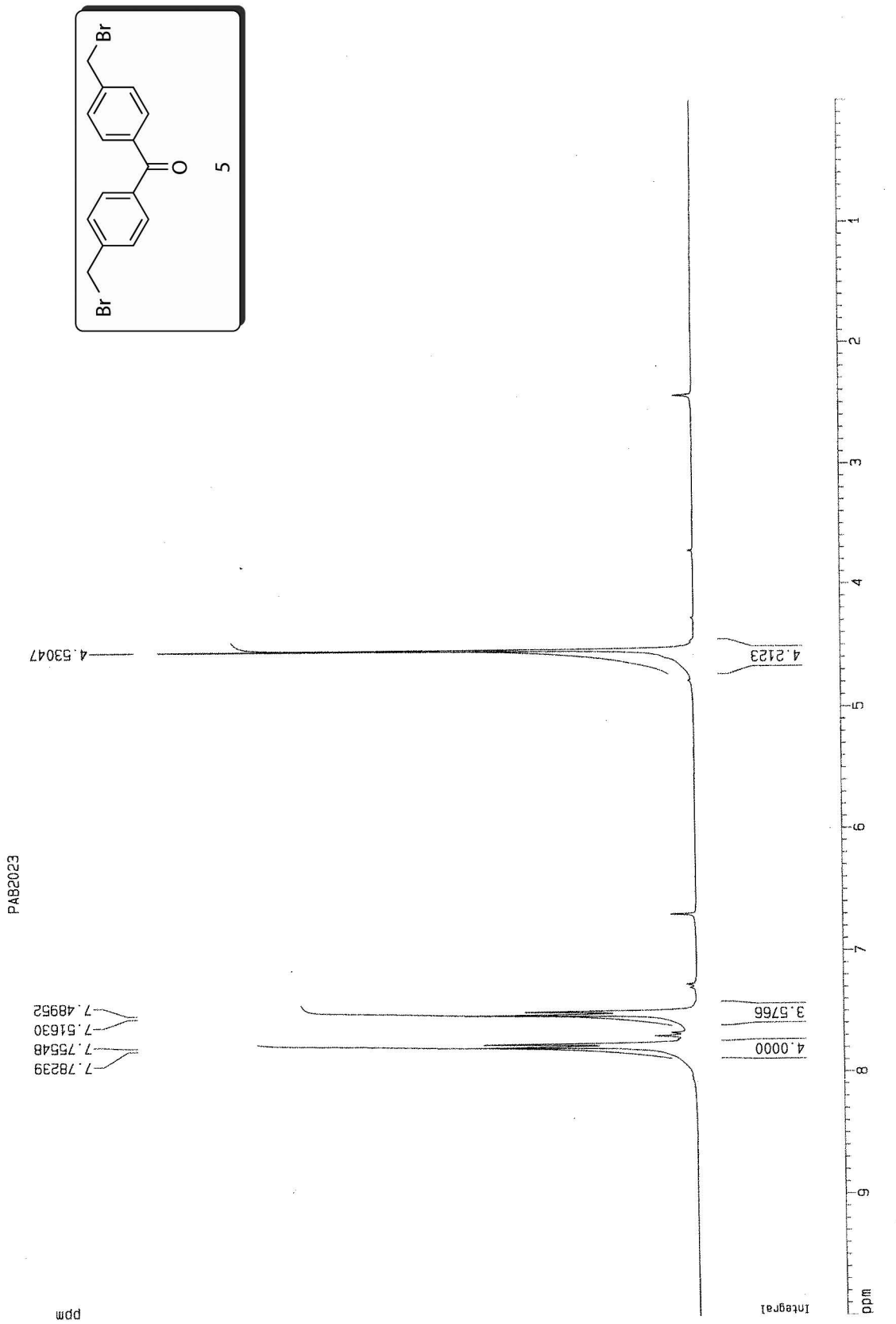
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ppm

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80
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140
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ppm

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4.5
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6.0
6.5
7.0
ppm
Integral
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4.000
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7.23842
7.22162
7.21175
7.10452
7.01350
6.99653
6.90346
6.88613
6.86326
6.84611
CD2Cl2
8

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12/18/05
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129.08
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131.74
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140.54
142.47
159.73
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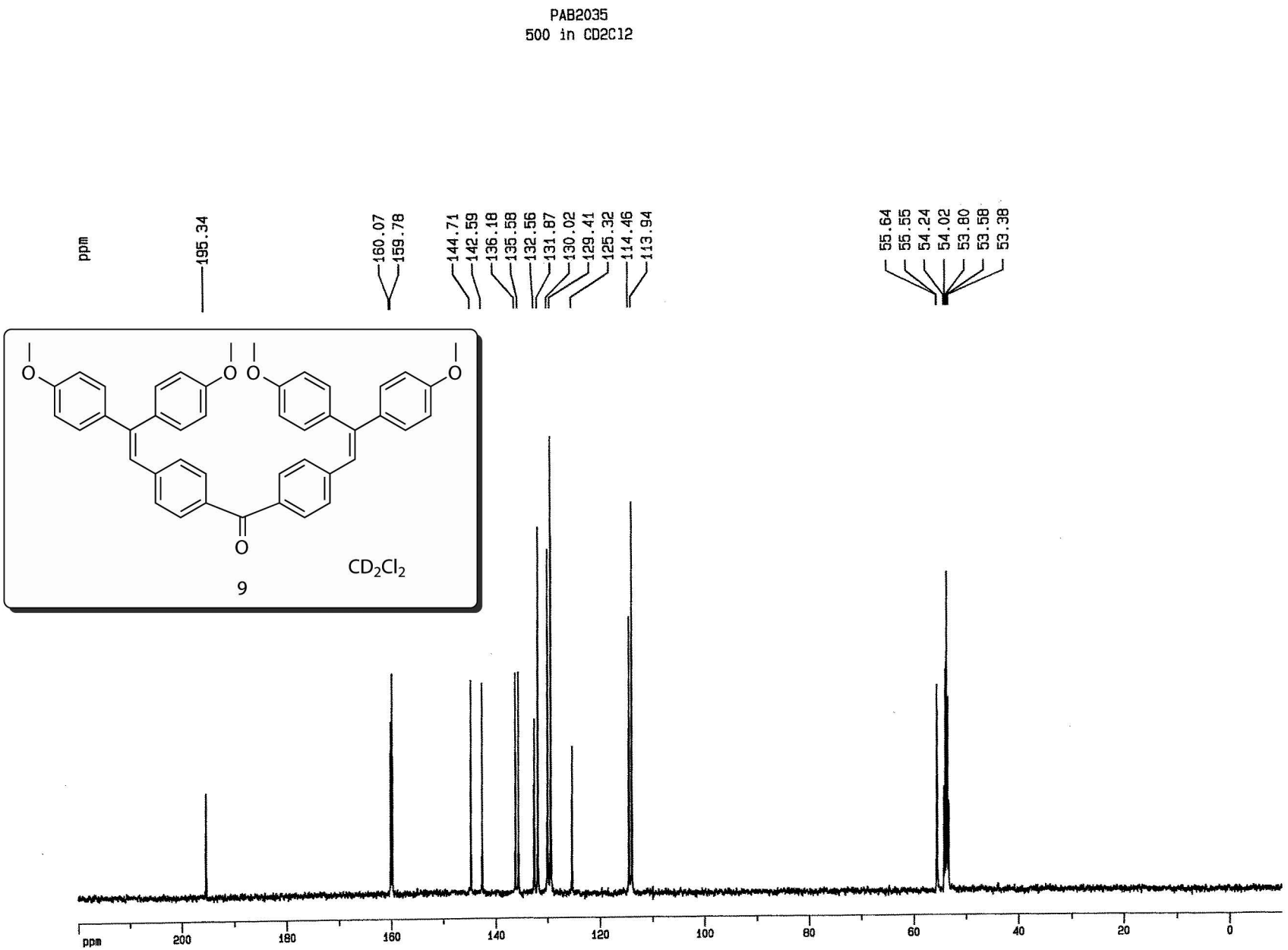
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53.58
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O
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O
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80
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20
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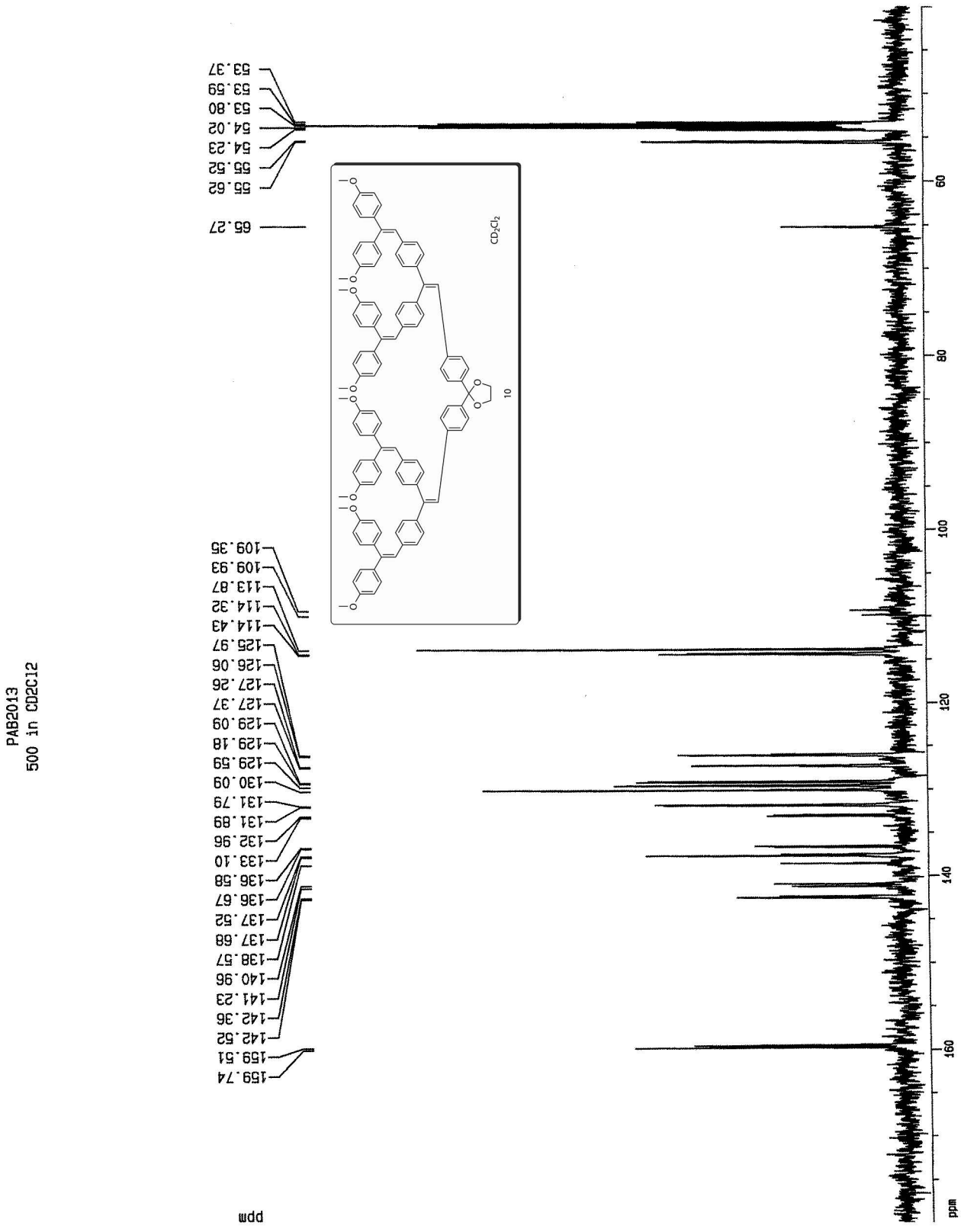
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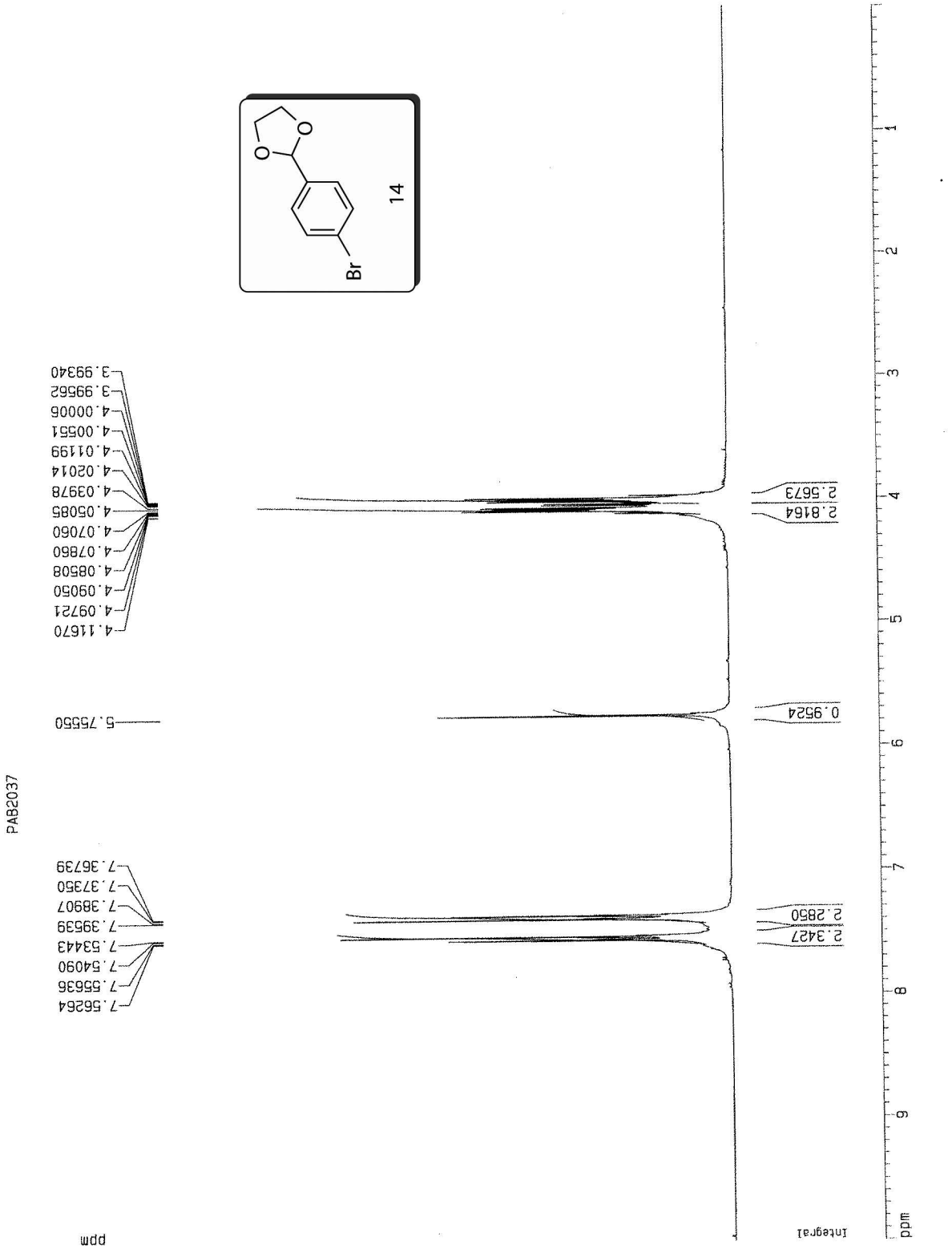
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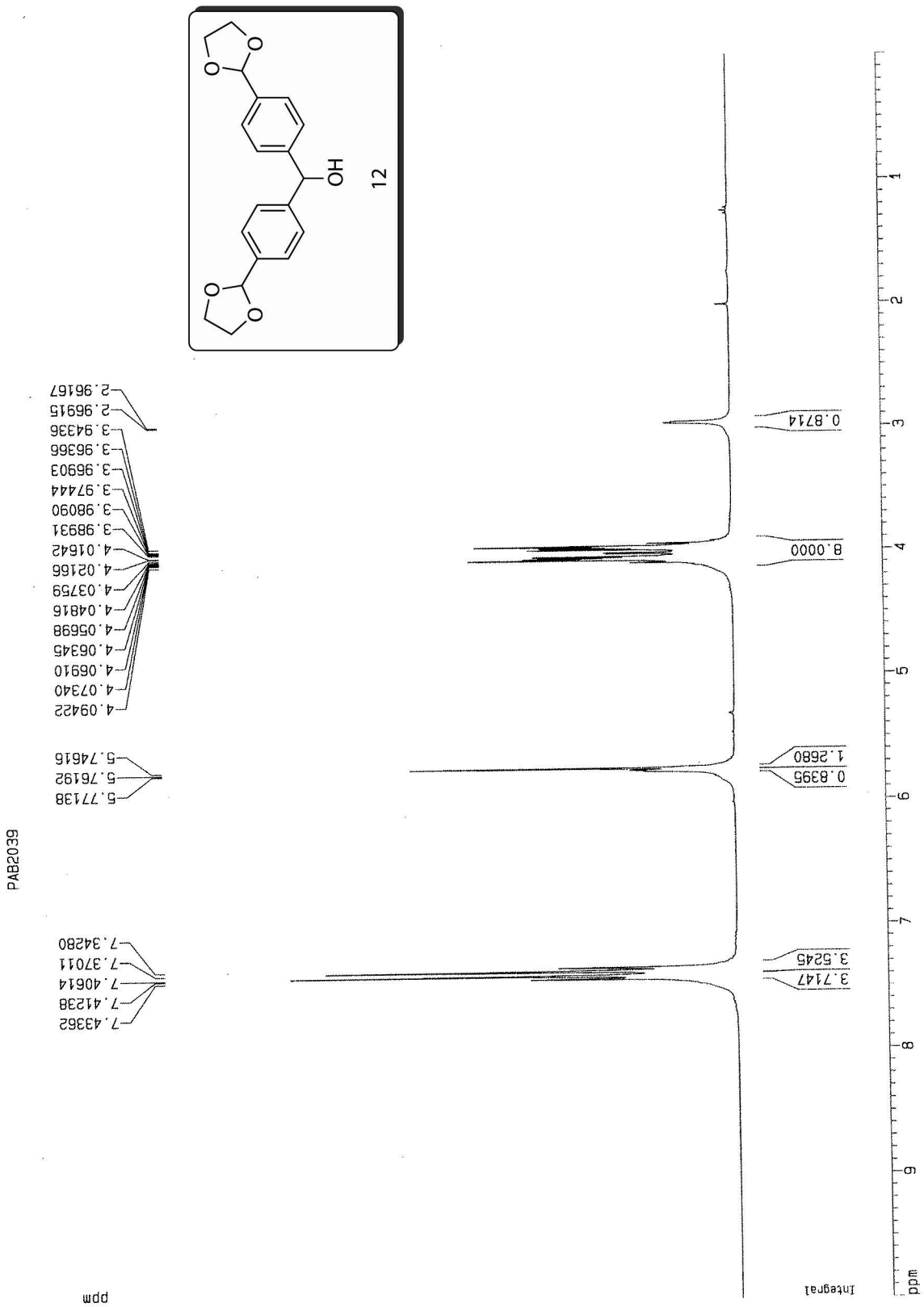
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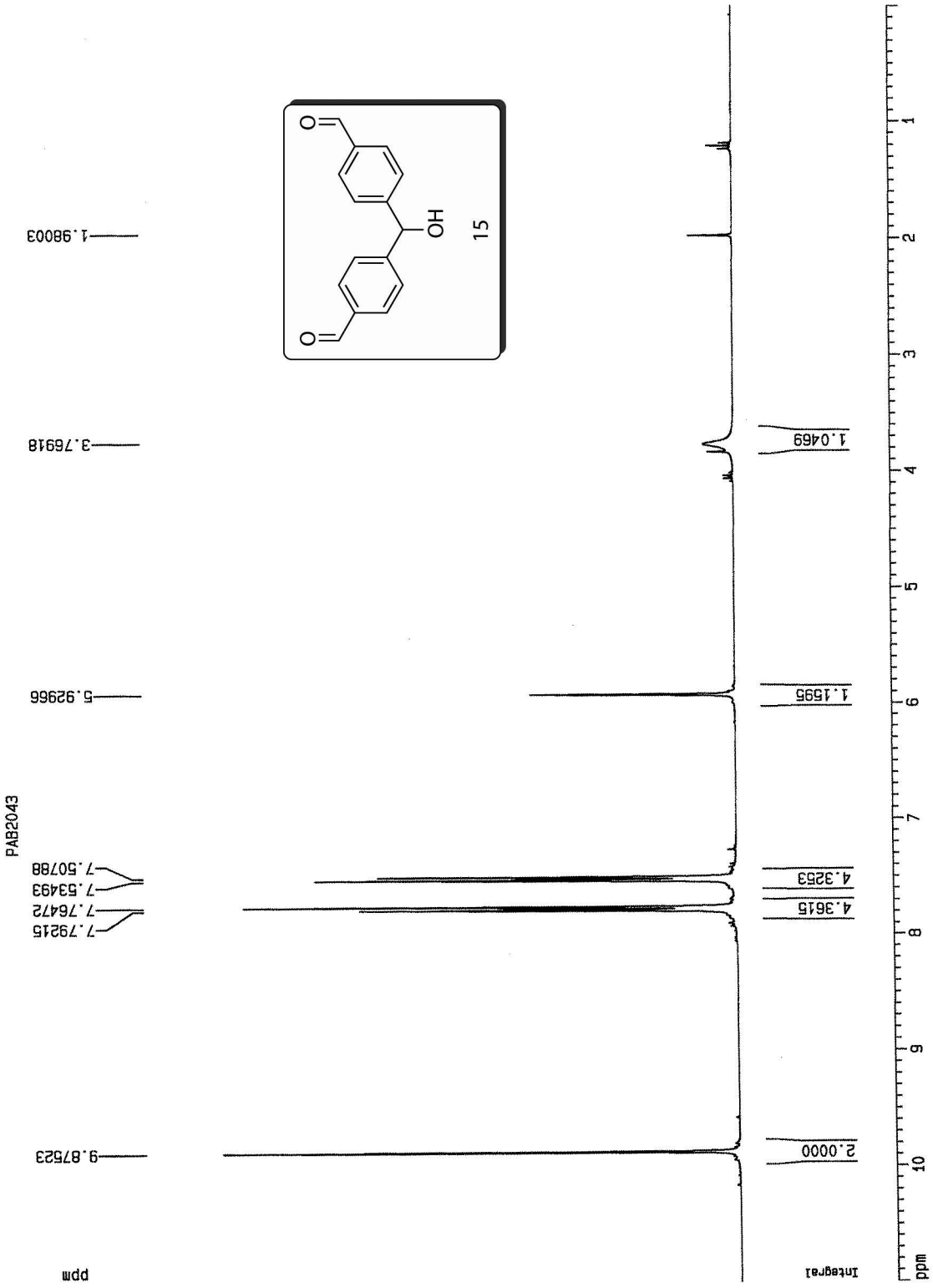
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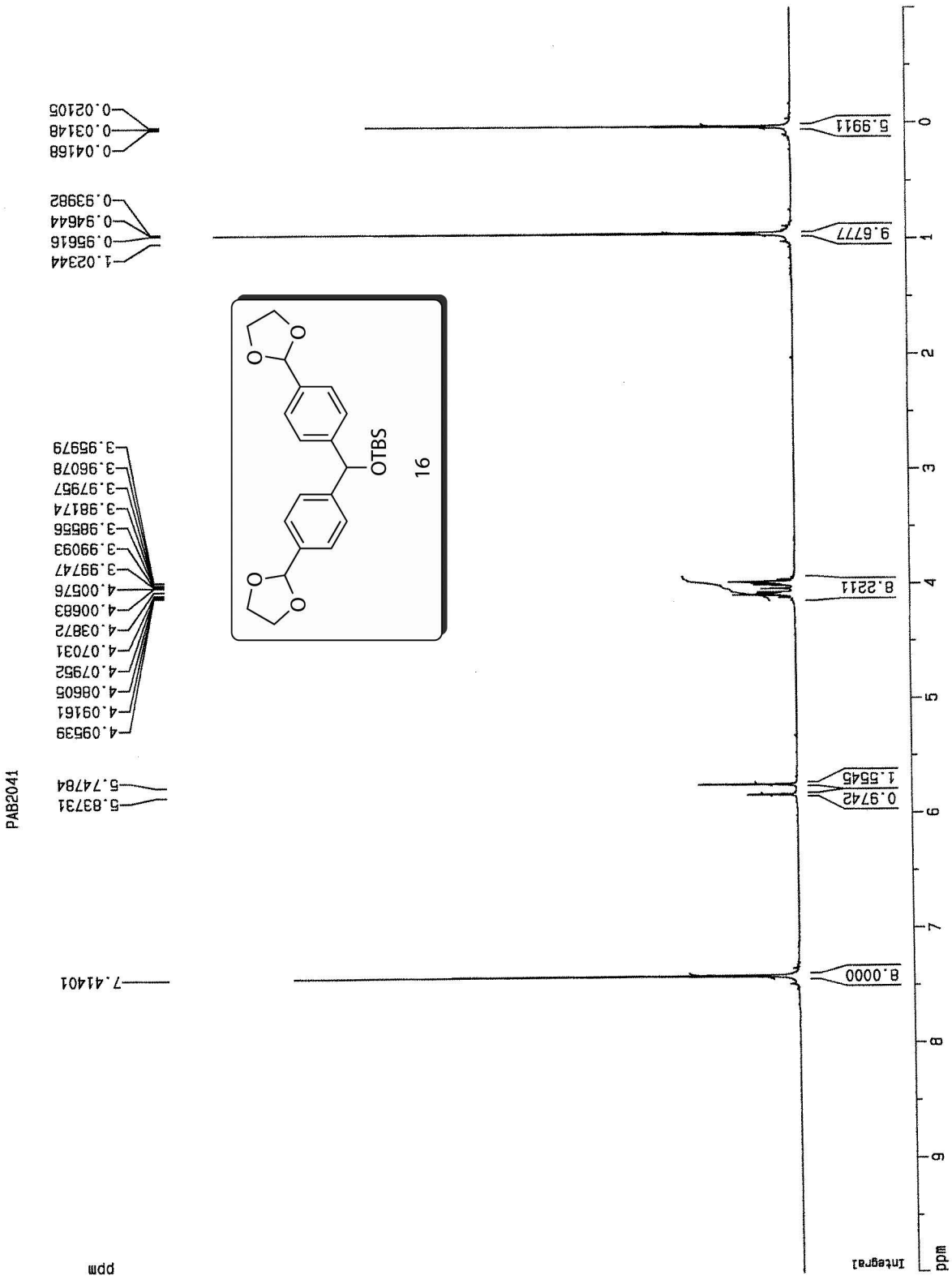
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ppm

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180
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ppm

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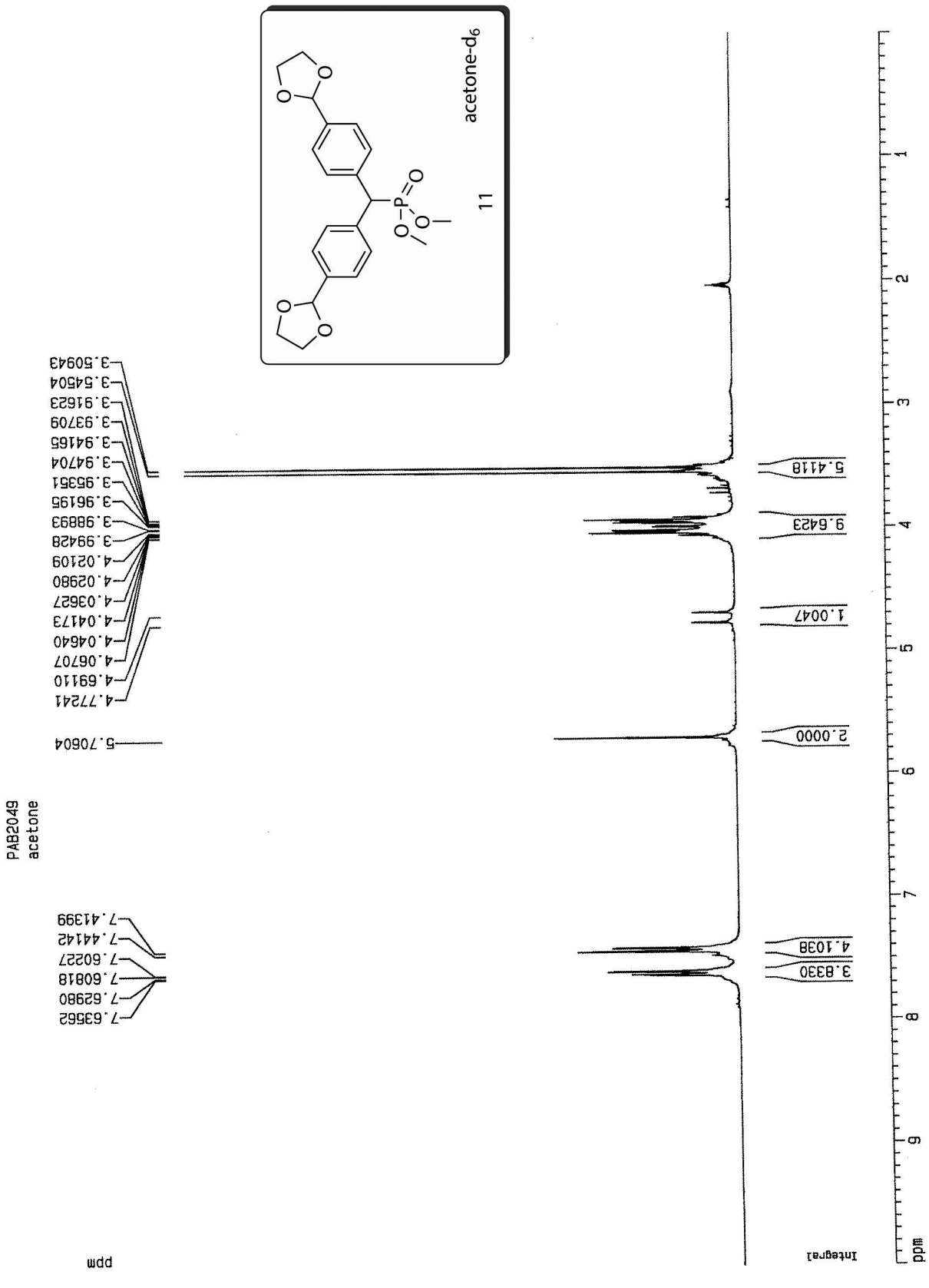
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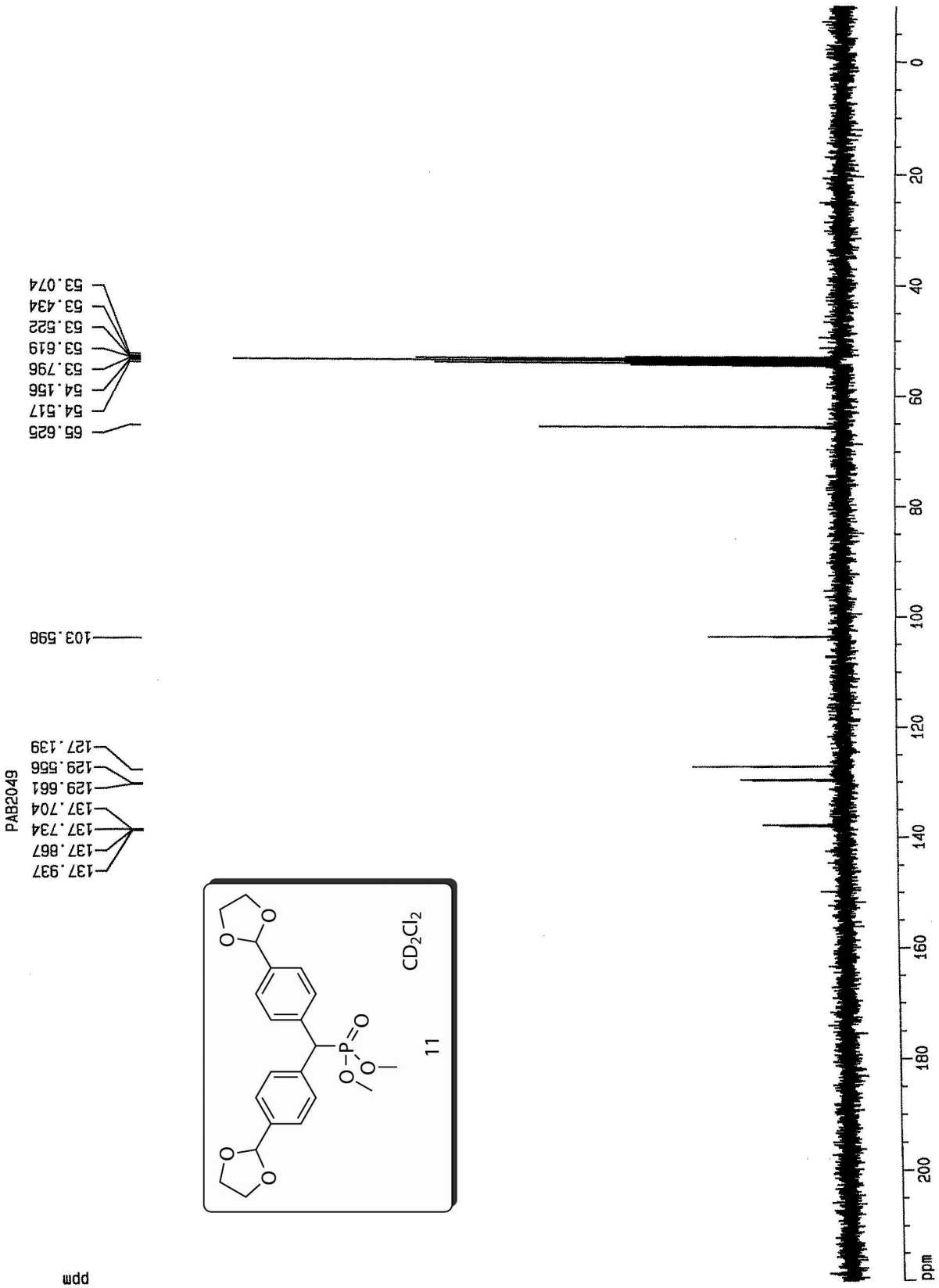
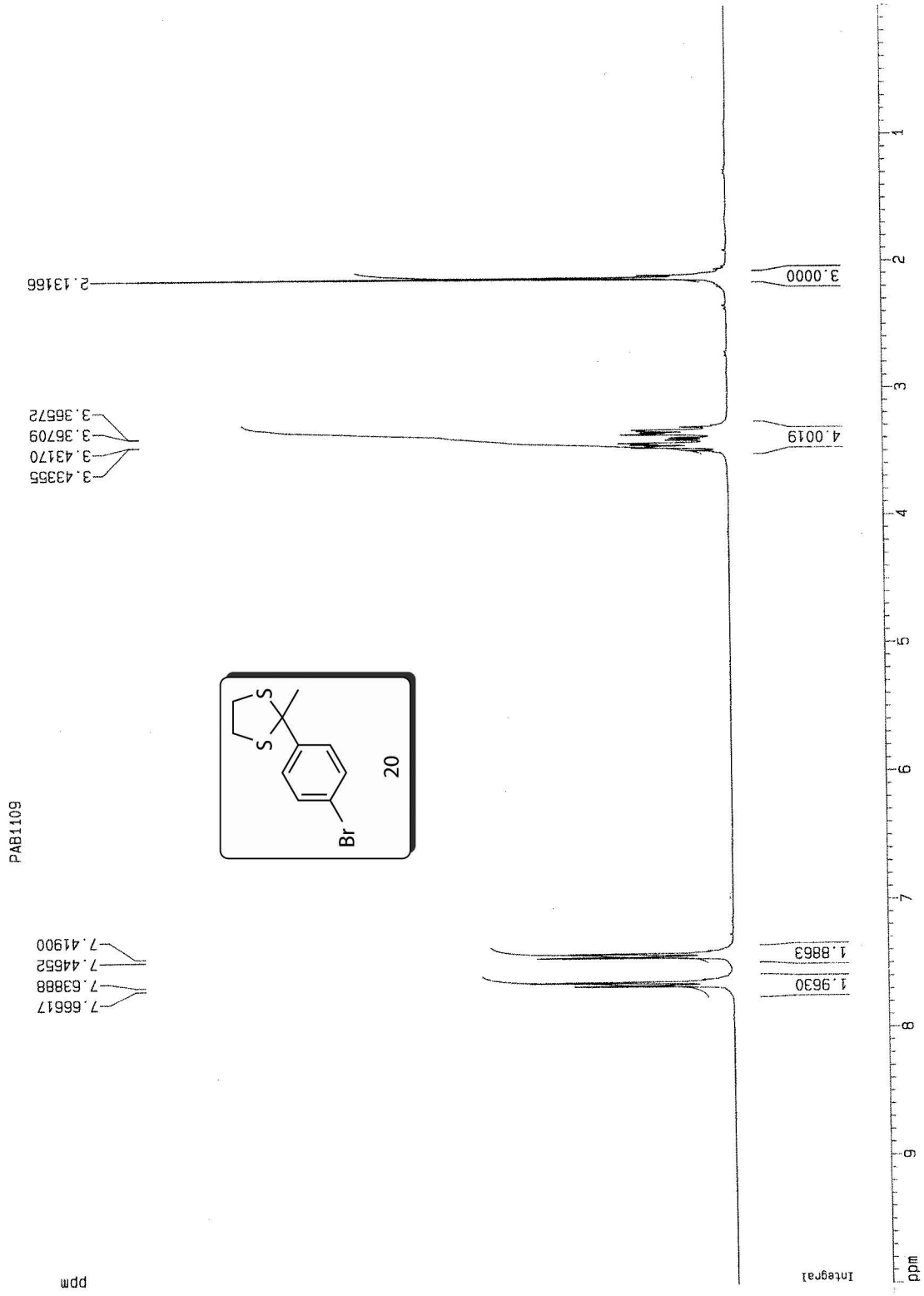

PAB2049
137.937
137.867
137.734
137.704
129.661
129.556
127.139
103.598
65.625
54.517
54.156
53.796
53.619
53.522
53.434
53.074
CD_2Cl_2
11
ppm

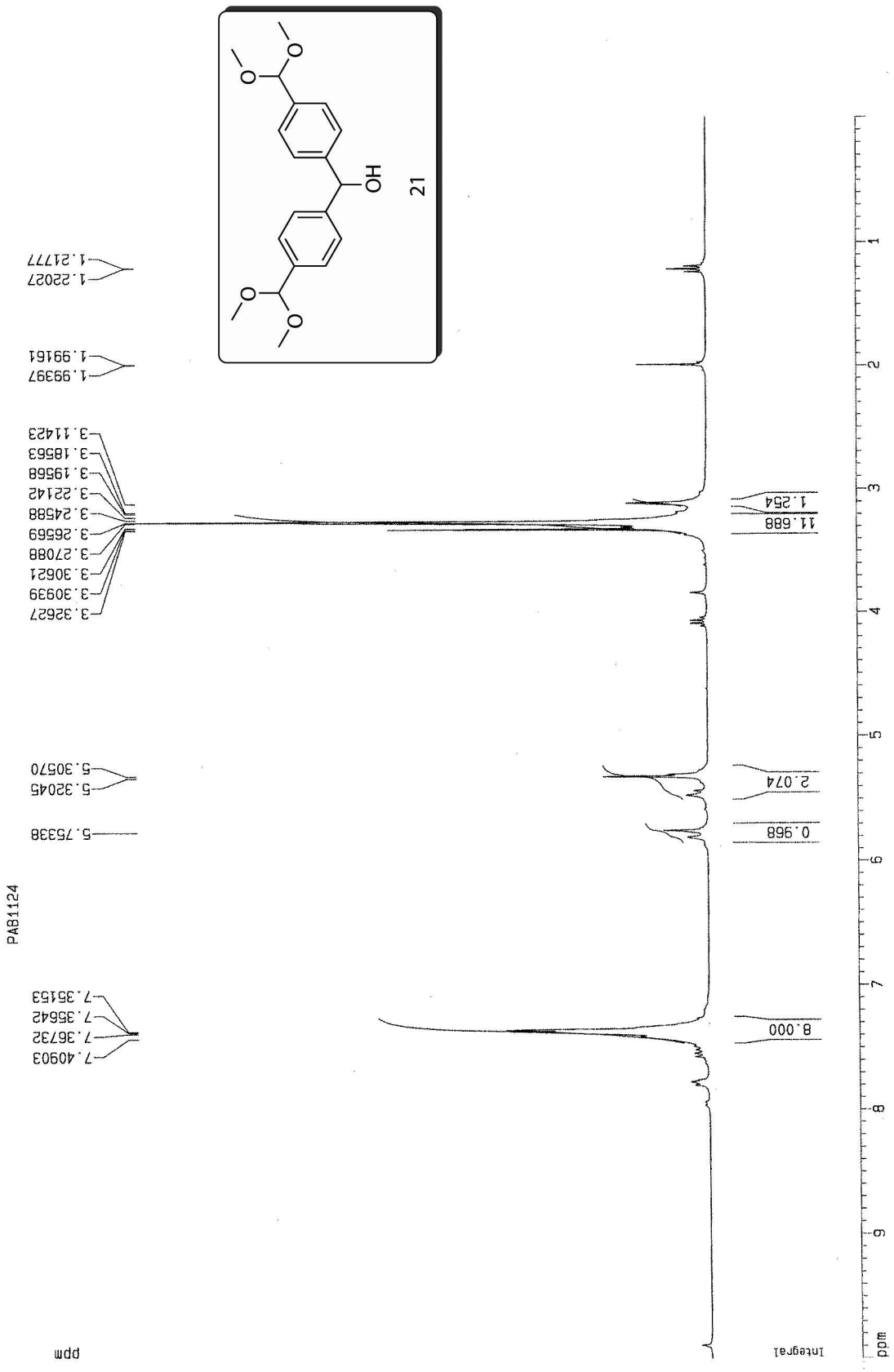
PAB2049
acetone
ppm
206.082
139.106
139.041
138.474
130.106
130.001
127.569
103.968
65.822
53.403
53.312
51.111
49.286
30.564
30.308
30.052
29.796
29.538
29.281
29.024
acetone-d6
11
0
20
40
60
80
100
120
140
160
180
200
ppm

PAB2051
ppm
Integral
0.0396
0.9012
6.265
8.974
19.108
3.959
1.028
6.347
3.834
3.899
4.068
4.090
4.343
7.4746
7.4476
7.4258
7.3980
7.3291
7.3014
7.2384
7.2113
7.1492
7.1215
7.0111
7.0007
6.9840
5.8096
5.7764
5.6286
4.1541
4.1144
4.0982
4.0594
4.0359
4.0011
OTBS
19
CD_2Cl_2

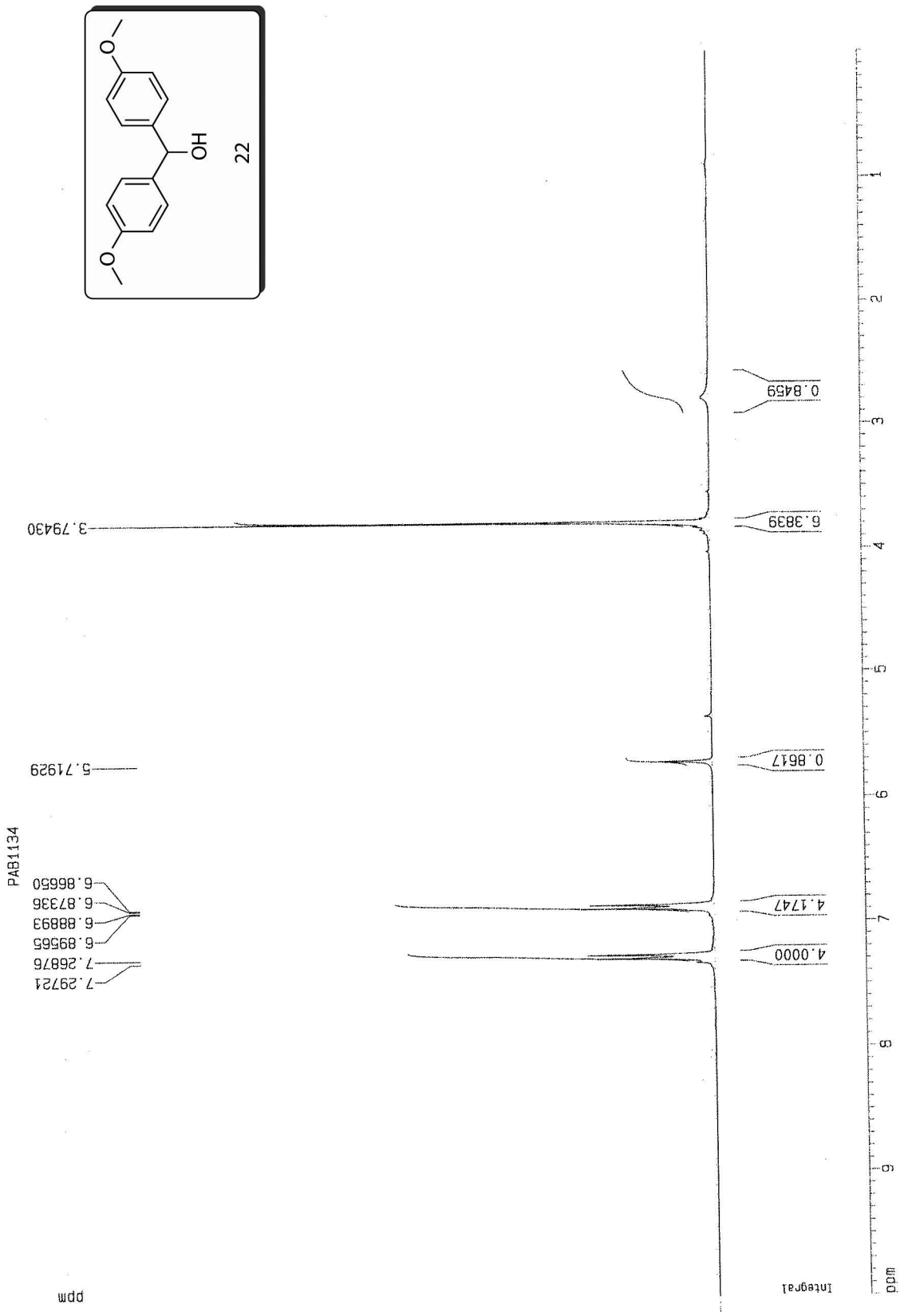
PAB2051
ppm
-4.706
14.287
18.549
23.064
26.021
31.994
53.084
53.443
53.805
54.164
54.532
65.737
65.778
76.606
103.871
103.988
126.322
126.779
127.364
127.875
128.909
129.847
130.657
136.387
137.856
141.673
141.880
144.340
144.661
OTBS
19
CD_2Cl_2
0
20
40
60
80
100
120
140
160
180
200
ppm


PAB1109
20
Br
S
S
ppm
Integral
2.13166
3.36572
3.36709
3.43170
3.43355
7.41900
7.44652
7.63888
7.66617
3.0000
4.0019
1.8863
1.9630
1
2
3
4
5
6
7
8
9
ppm

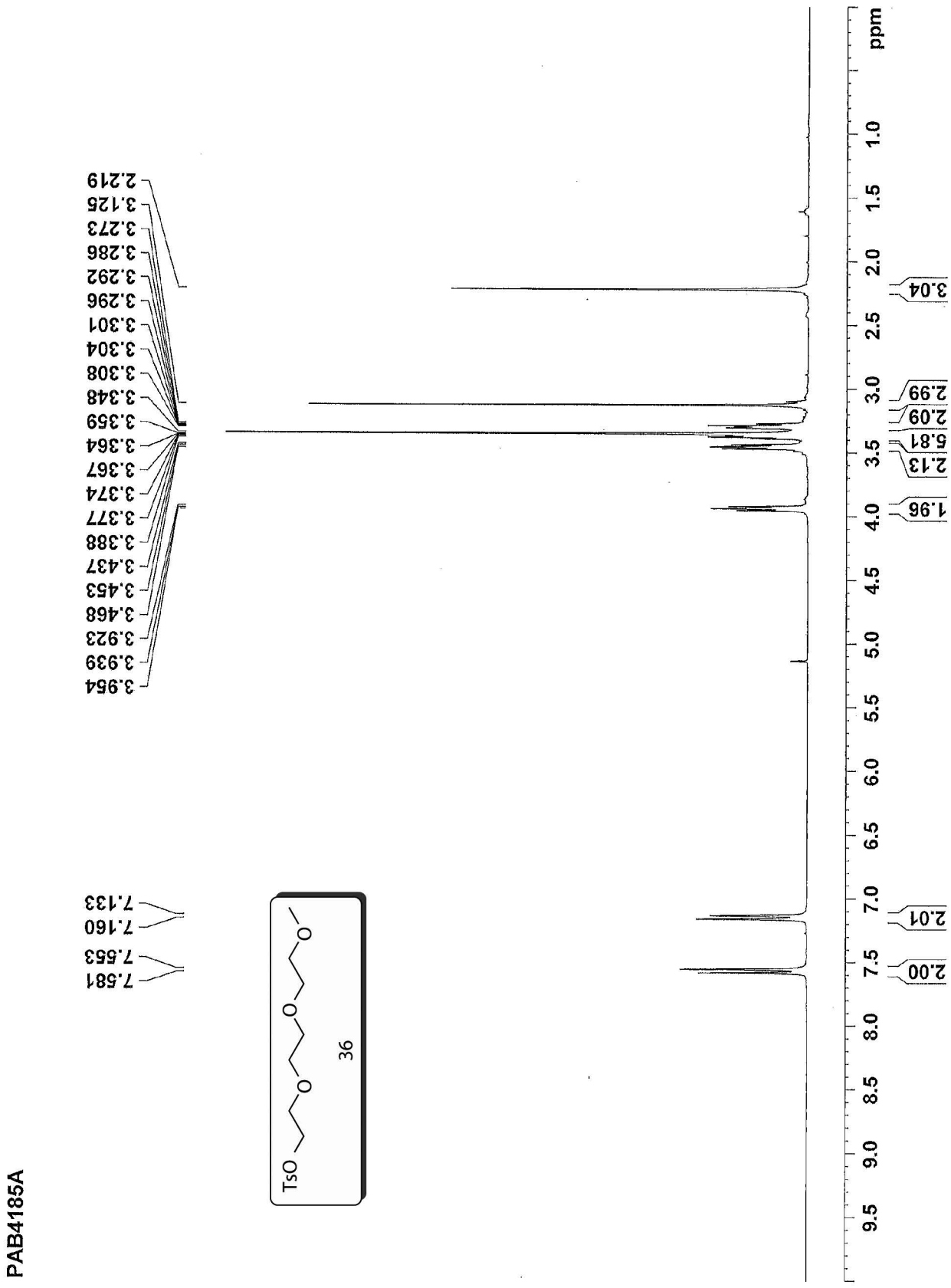
PAB1109
33.331
40.221
67.791
76.560
76.982
77.406
120.818
128.510
130.737
145.044
ppm
0
20
40
60
80
100
120
140
160
180
200
ppm
S
S
Br
20

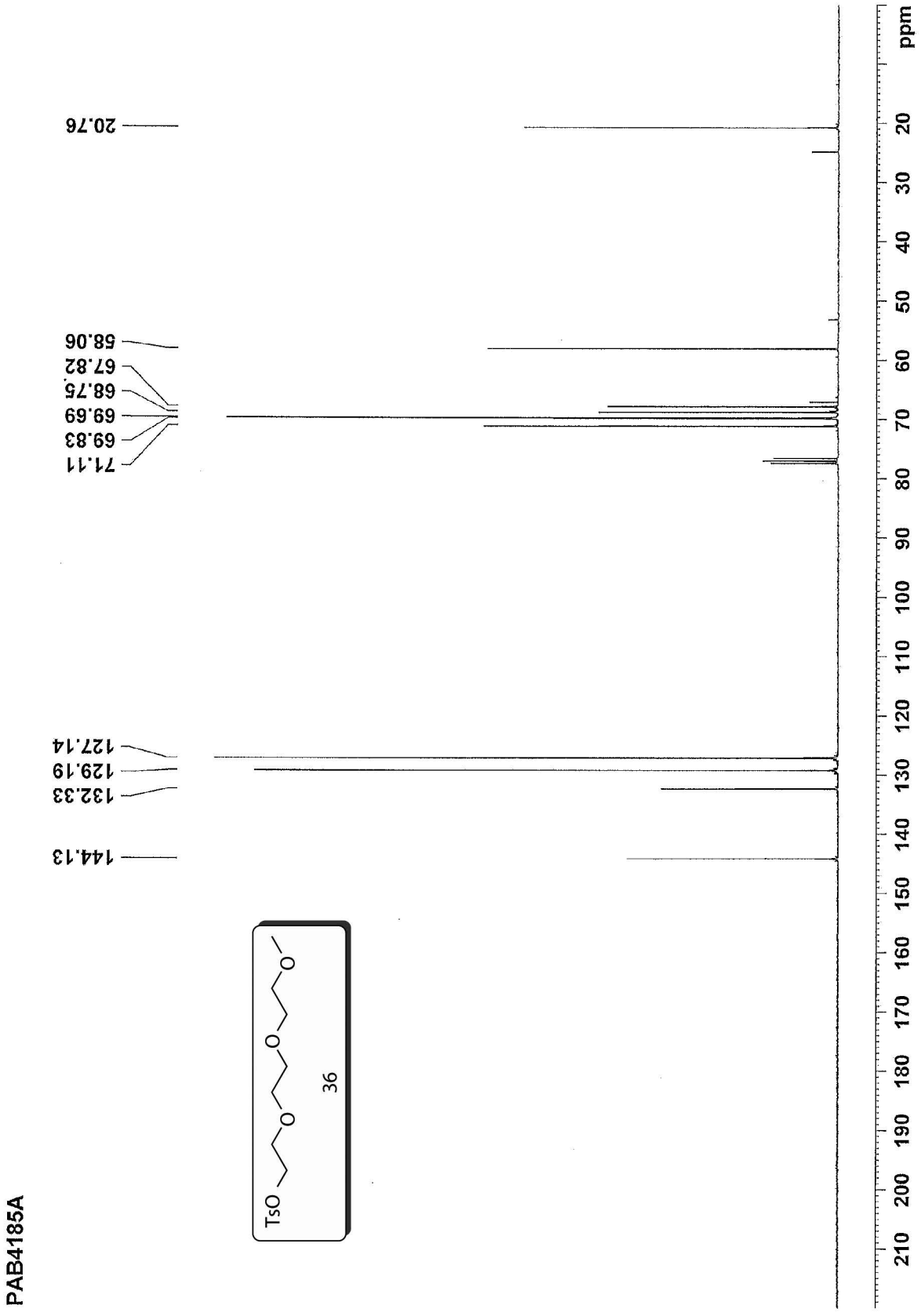

21
OH
PAB1124
ppm
Integral
1.22027
1.21777
1.99397
1.99161
3.11423
3.18563
3.19568
3.22142
3.24588
3.26569
3.27088
3.30621
3.30939
3.32627
5.30570
5.32045
5.75338
7.35153
7.35642
7.36732
7.40903
1.254
11.688
2.074
0.968
8.000

PAB1124
144.146
136.921
127.109
126.769
126.663
126.535
126.201
102.794
77.418
76.995
76.569
75.312
52.521
52.434
50.105
13.917
ppm
OH
21
0
20
40
60
80
100
120
140
160
180
200
ppm

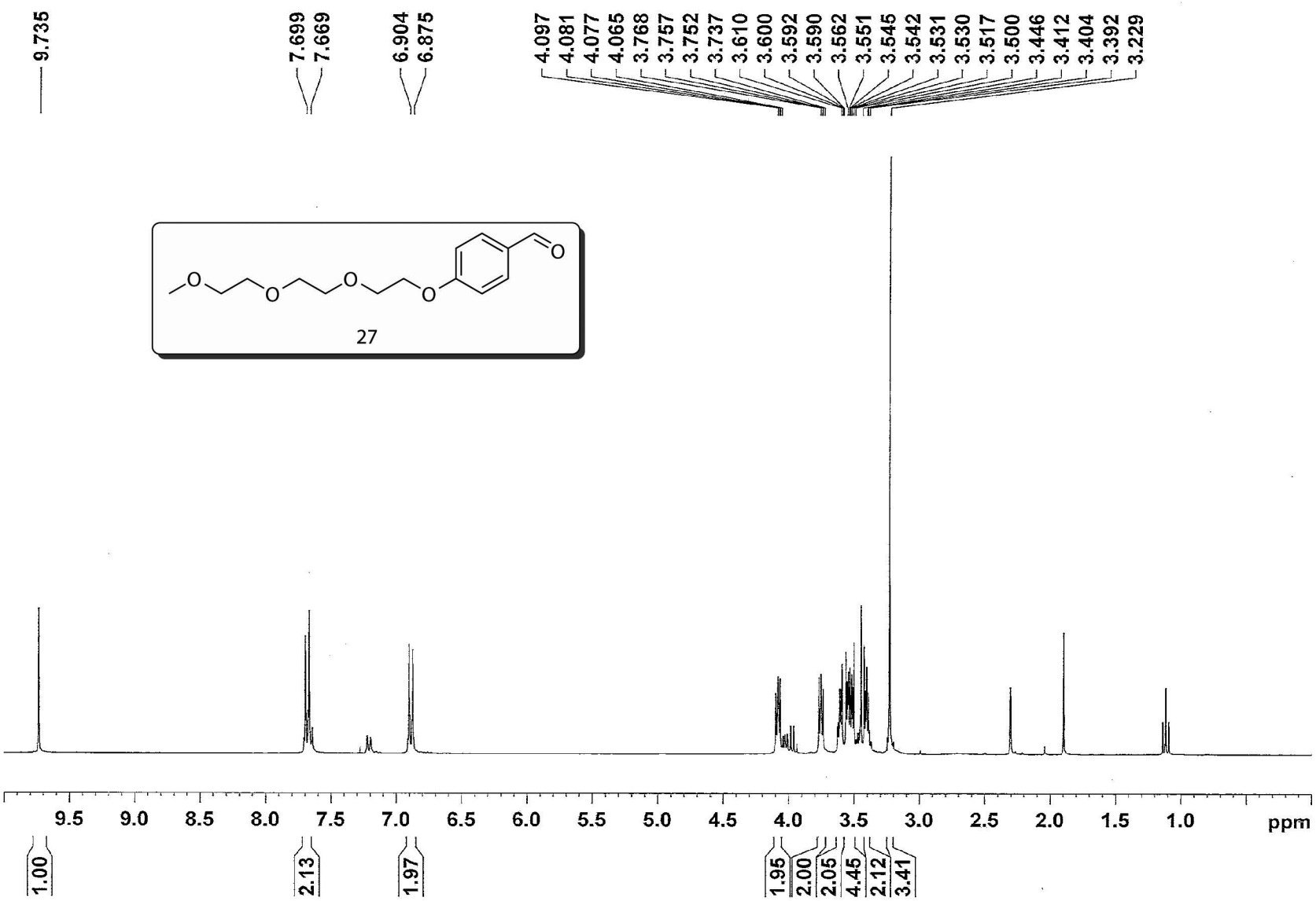

22
PAB1134
7.29721
7.26876
6.89565
6.88893
6.87336
6.86650
5.71929
3.79430
4.1747
4.0000
0.8617
6.3839
0.8459
ppm
Integral

22
55.080
75.097
113.632
127.608
128.309
136.376
158.730
PAB1134
ppm

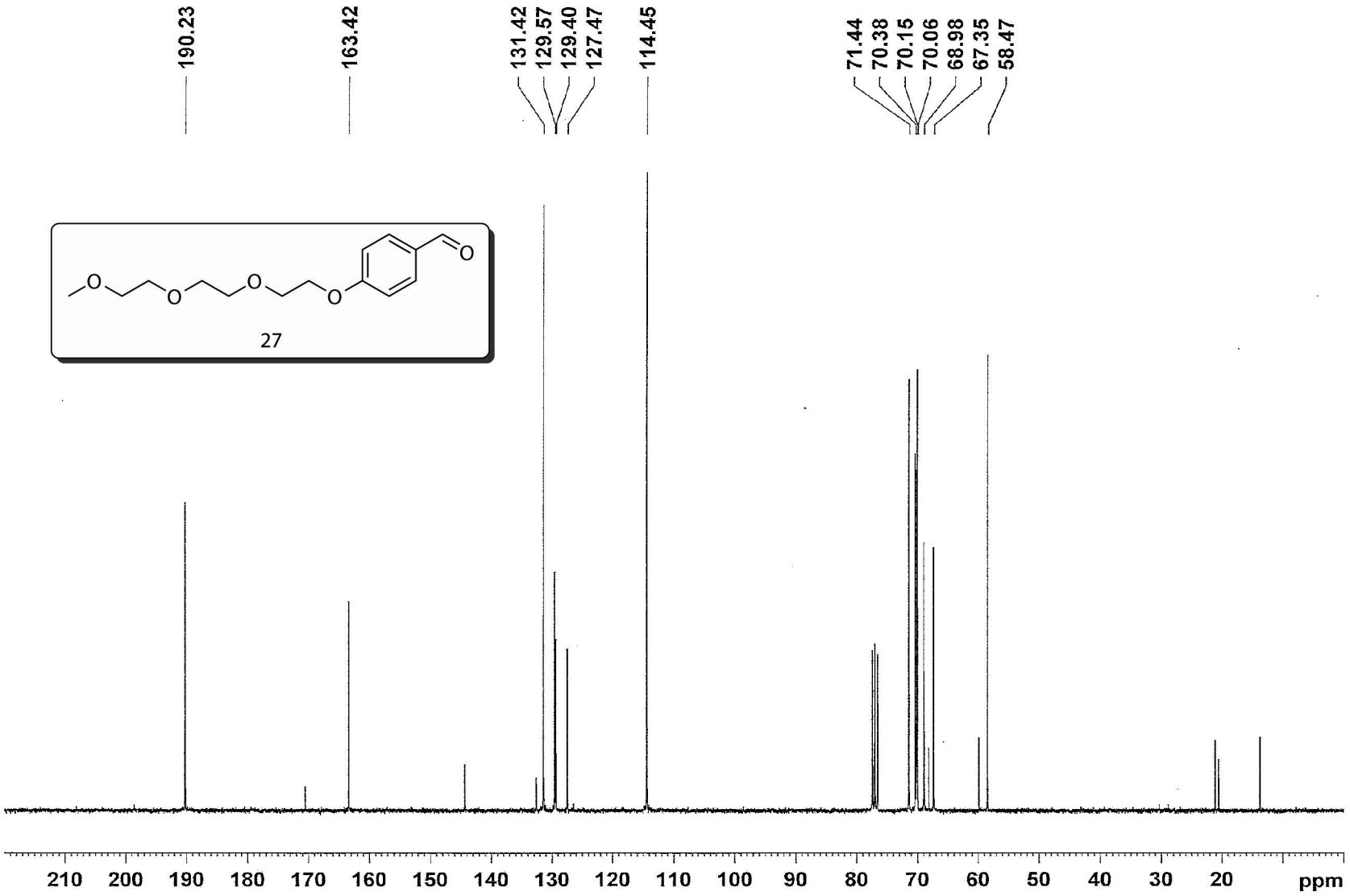

PAB4185A
TsO
36
7.581
7.563
7.160
7.133
3.964
3.939
3.923
3.468
3.453
3.437
3.388
3.377
3.374
3.367
3.364
3.359
3.348
3.308
3.304
3.301
3.296
3.292
3.286
3.273
3.125
2.219
2.00
2.01
1.96
2.13
5.81
2.09
2.99
3.04
ppm


PAB4185A
TsO
O
O
O
O
36
144.13
132.33
129.19
127.14
71.11
69.83
69.69
68.75
67.82
58.06
20.76
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

PAB5015C

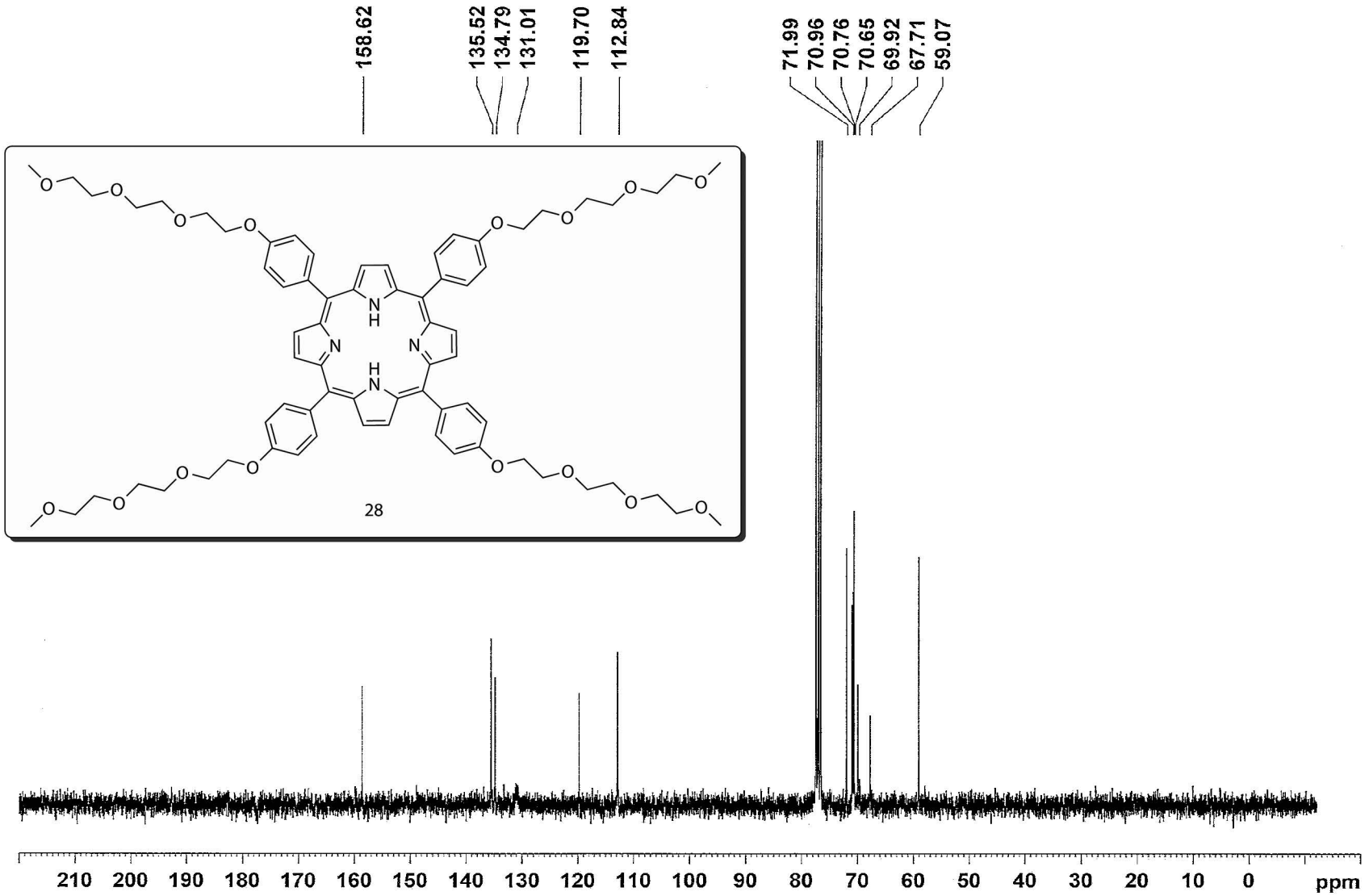

9.735
7.699
7.669
6.904
6.875
4.097
4.081
4.077
4.065
3.768
3.757
3.752
3.737
3.610
3.600
3.592
3.590
3.562
3.551
3.545
3.542
3.531
3.530
3.517
3.500
3.446
3.412
3.404
3.392
3.229
27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.13
1.97
1.95
2.00
2.05
4.45
2.12
3.41

PAB5015C

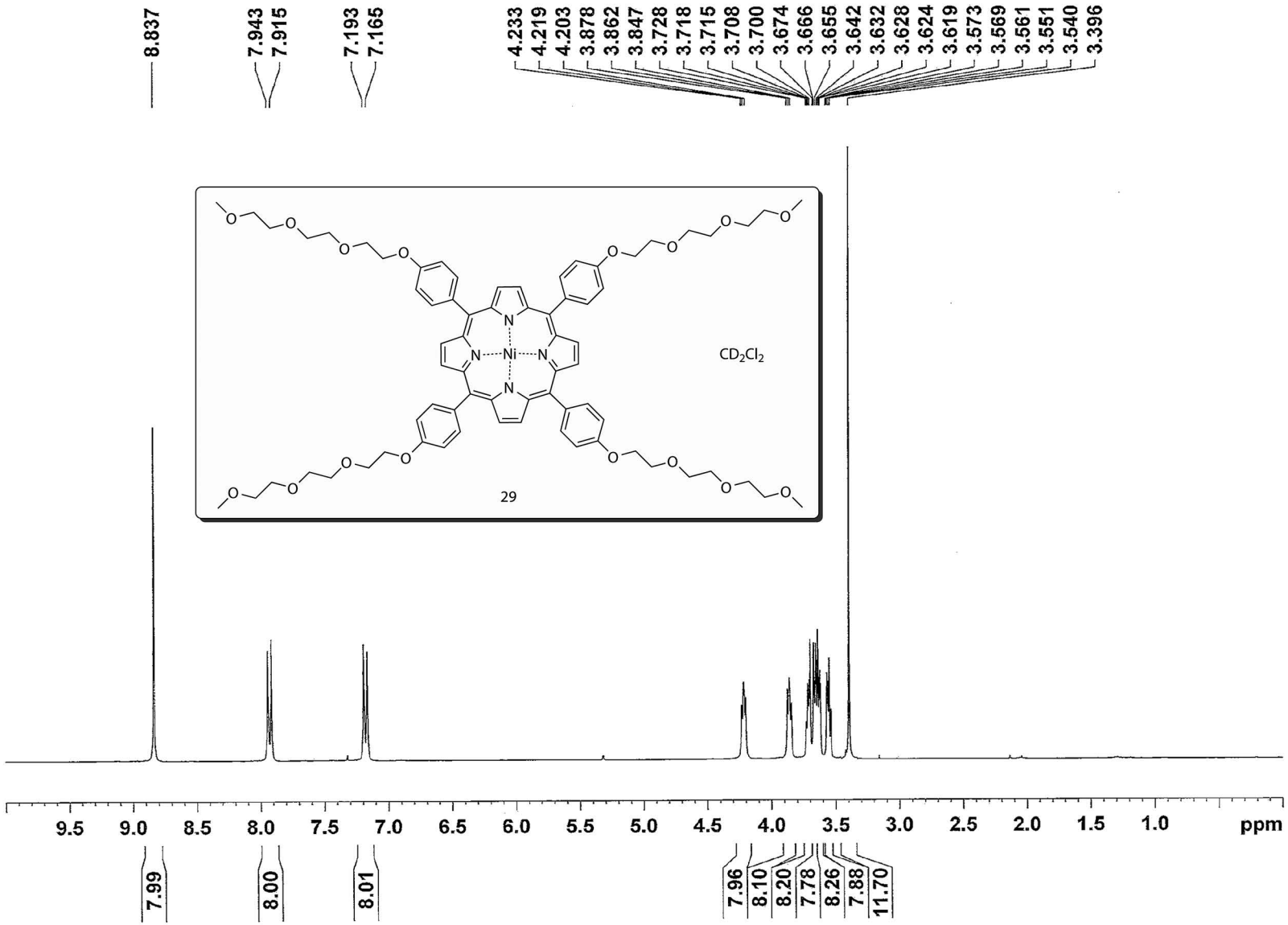

190.23
163.42
131.42
129.57
129.40
127.47
114.45
71.44
70.38
70.15
70.06
68.98
67.35
58.47
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

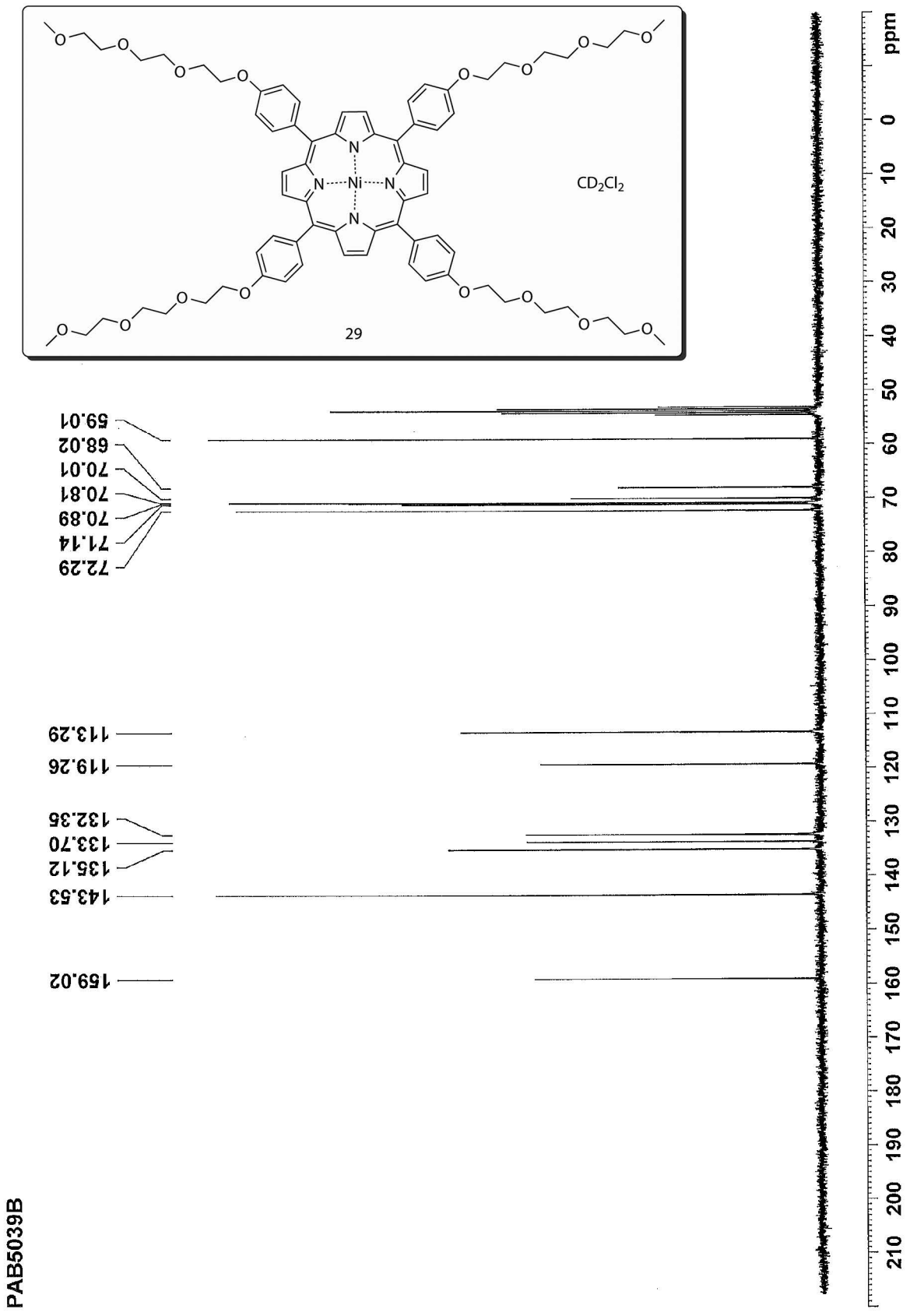
PAB5029A
-2.739
3.440
3.619
3.633
3.640
3.650
3.741
3.751
3.758
3.772
3.791
3.803
3.811
3.820
3.825
3.874
3.879
3.888
3.896
3.908
4.047
4.063
4.079
4.414
4.431
4.446
7.289
7.317
8.108
8.136
8.873
28
ppm
1.88
8.00
7.92
8.03
7.74
7.94
8.81
8.30
8.70
8.18
11.28

PAB5029A

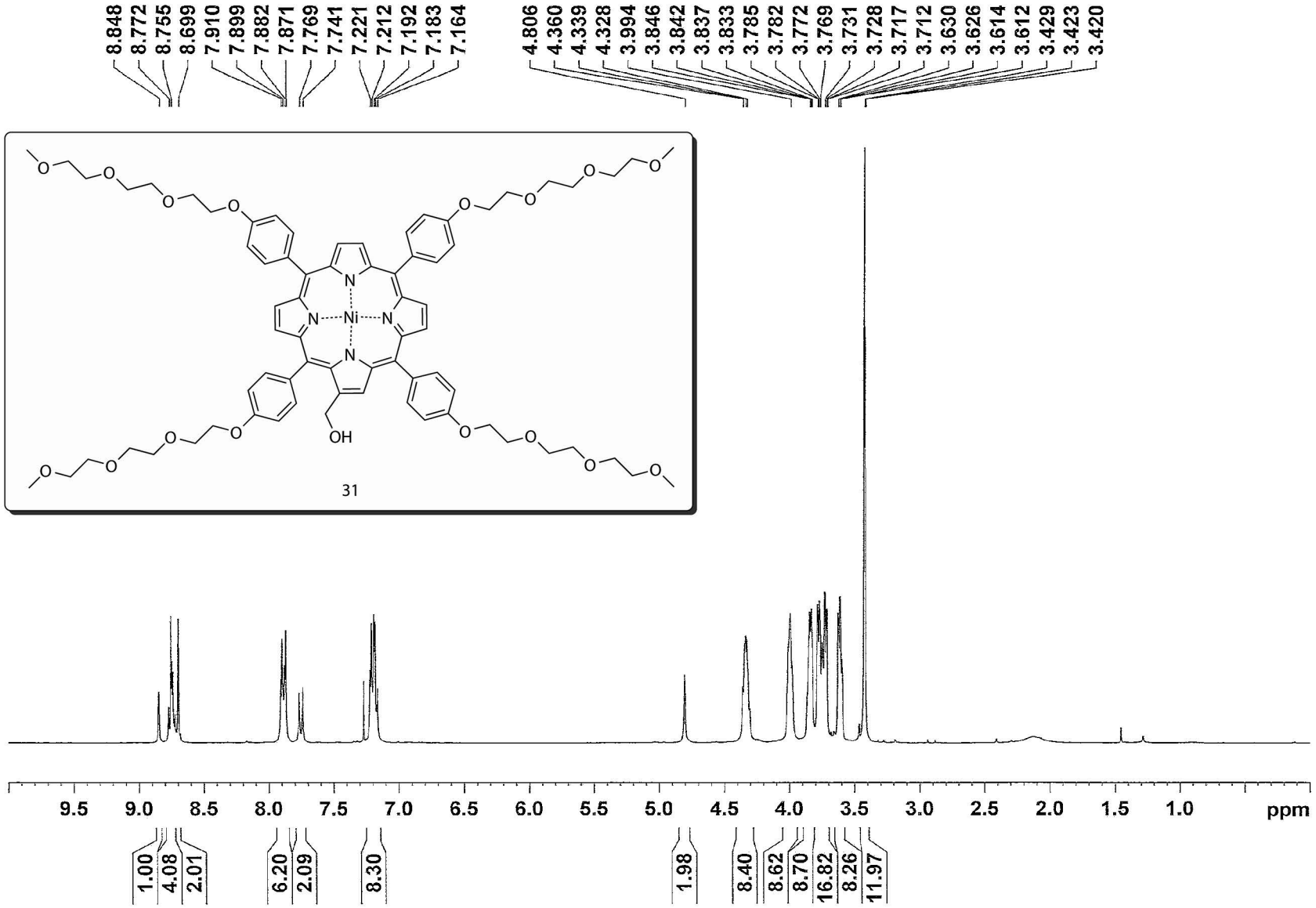

158.62
135.52
134.79
131.01
119.70
112.84
71.99
70.96
70.76
70.65
69.92
67.71
59.07
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

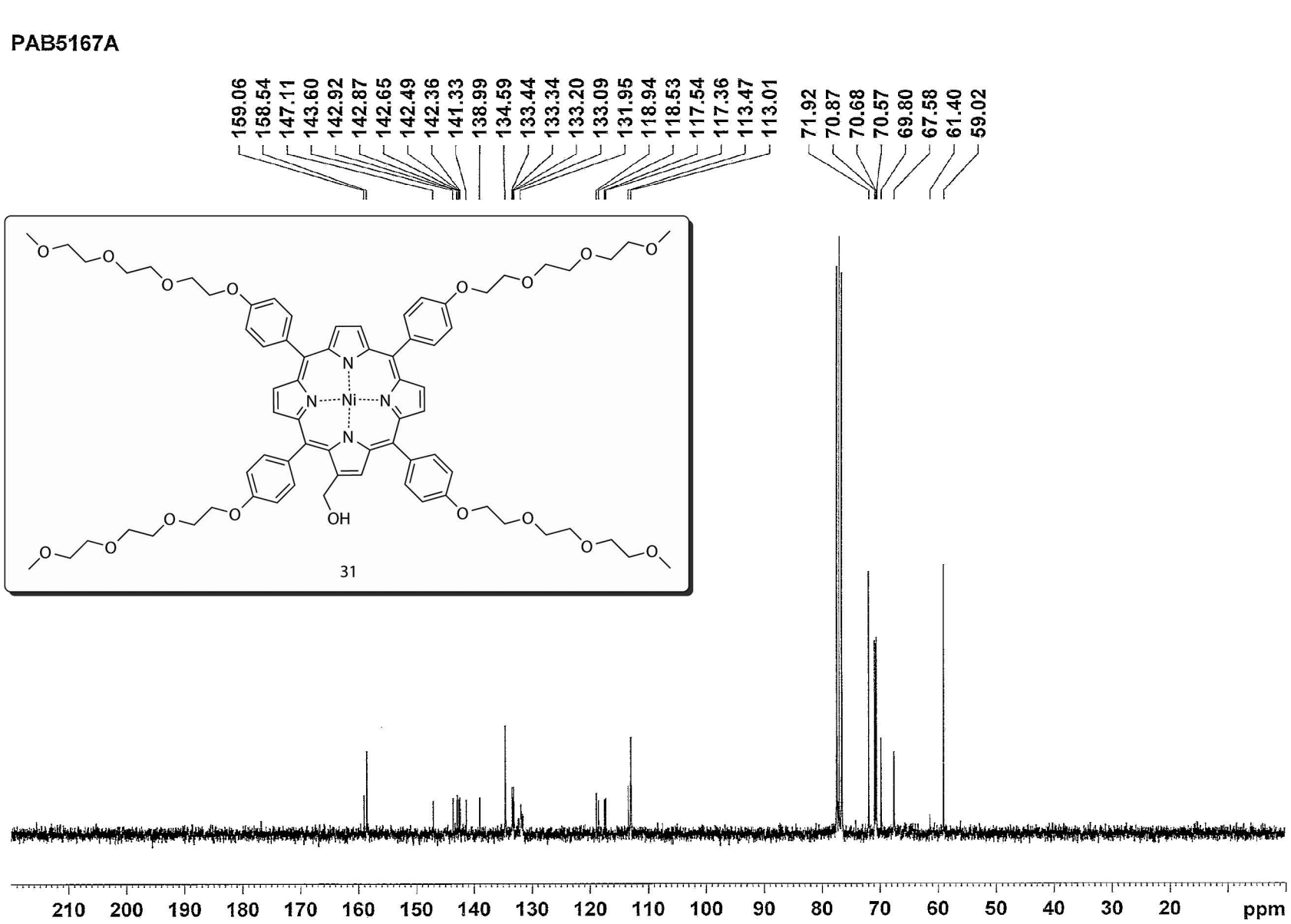
PAB5039B


8.837
7.943
7.915
7.193
7.165
4.233
4.219
4.203
3.878
3.862
3.847
3.728
3.718
3.715
3.708
3.700
3.674
3.666
3.655
3.642
3.632
3.628
3.624
3.619
3.573
3.569
3.561
3.551
3.540
3.396
N
Ni
N
N
CD2Cl2
29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
7.99
8.00
8.01
7.96
8.10
8.20
7.78
8.26
7.88
11.70

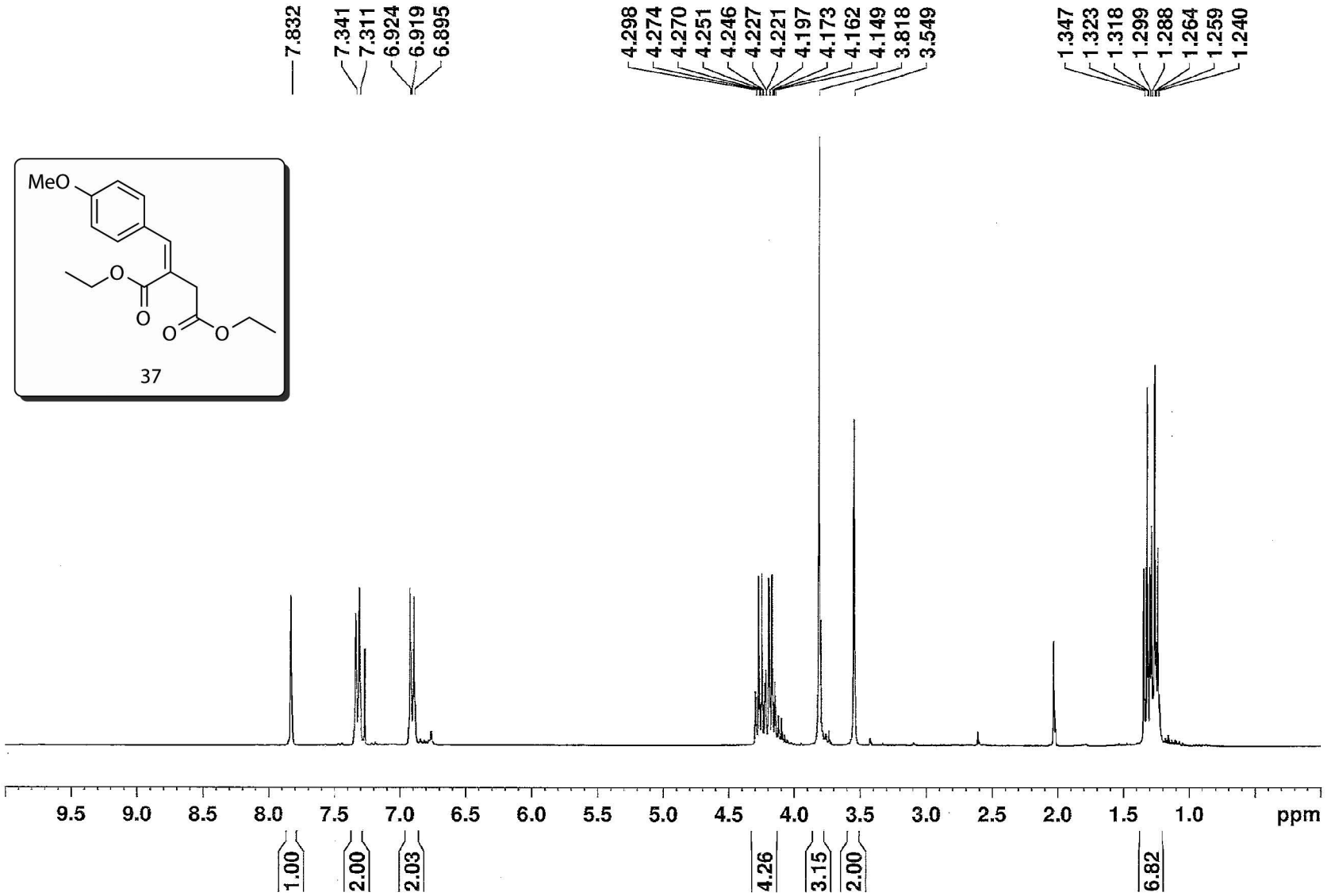

PAB5039B
29
CD_2Cl_2
159.02
143.53
135.12
133.70
132.36
119.26
113.29
72.29
71.14
70.89
70.81
70.01
68.02
59.01
ppm

PAB5167A

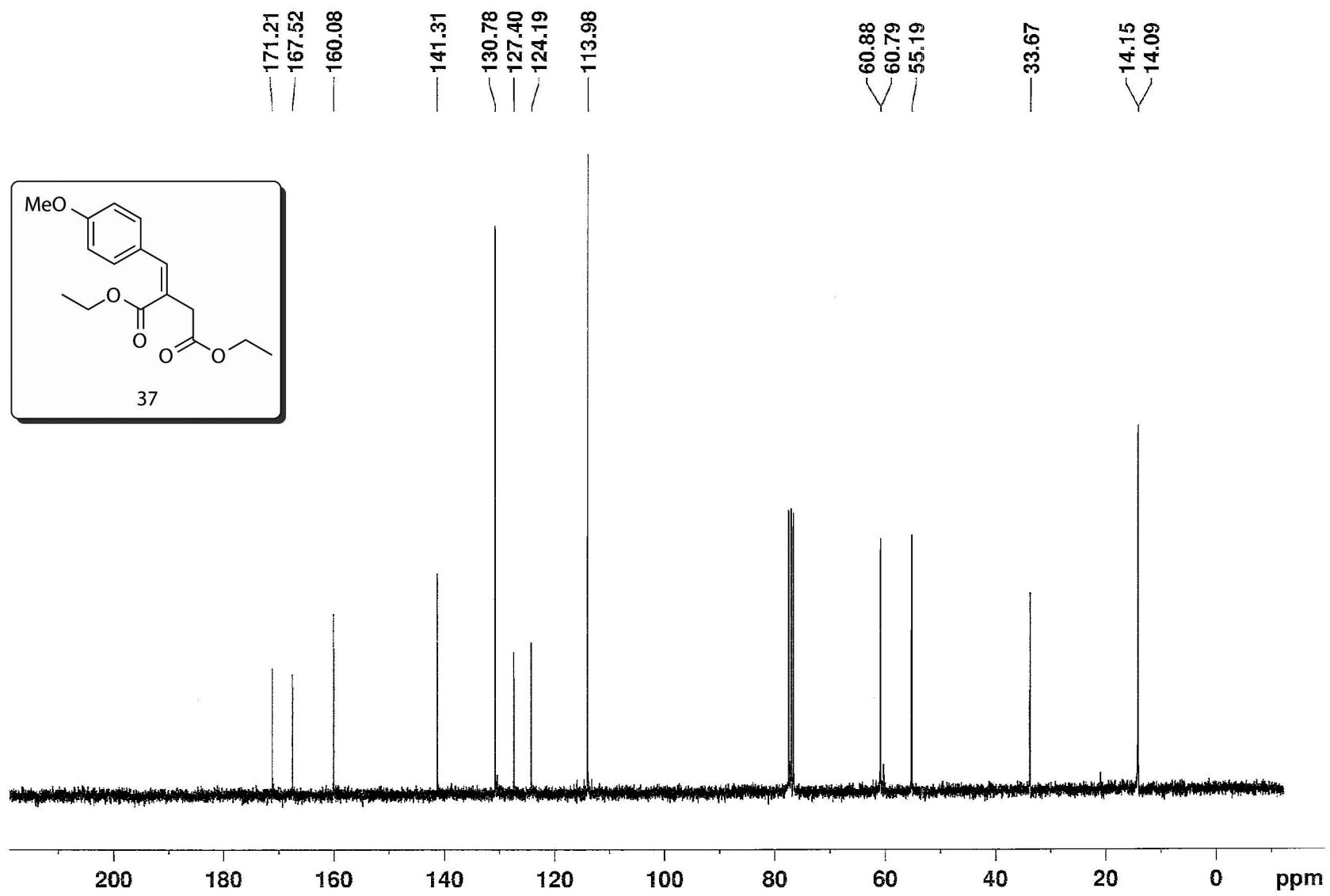

8.848
8.772
8.755
8.699
7.910
7.899
7.882
7.871
7.769
7.741
7.221
7.212
7.192
7.183
7.164
4.806
4.360
4.339
4.328
3.994
3.846
3.842
3.837
3.833
3.785
3.782
3.772
3.769
3.731
3.728
3.717
3.712
3.630
3.626
3.614
3.612
3.429
3.423
3.420
N
Ni
N
N
OH
31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
4.08
2.01
6.20
2.09
8.30
1.98
8.40
8.62
8.70
16.82
8.26
11.97

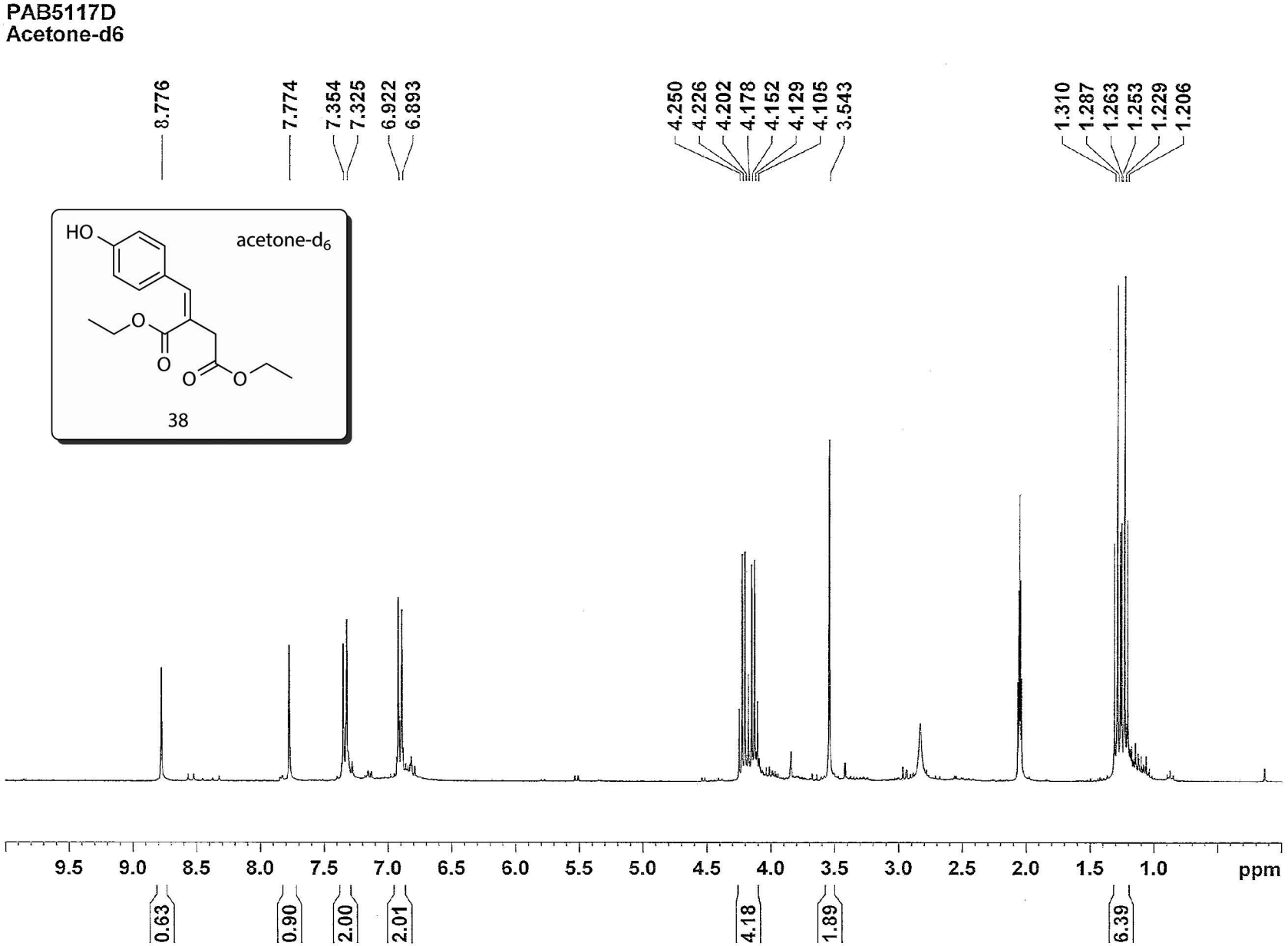

PAB5167A
159.06
158.54
147.11
143.60
142.92
142.87
142.65
142.49
142.36
141.33
138.99
134.59
133.44
133.34
133.20
133.09
131.95
118.94
118.53
117.54
117.36
113.47
113.01
71.92
70.87
70.68
70.57
69.80
67.58
61.40
59.02
N
Ni
N
N
OH
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

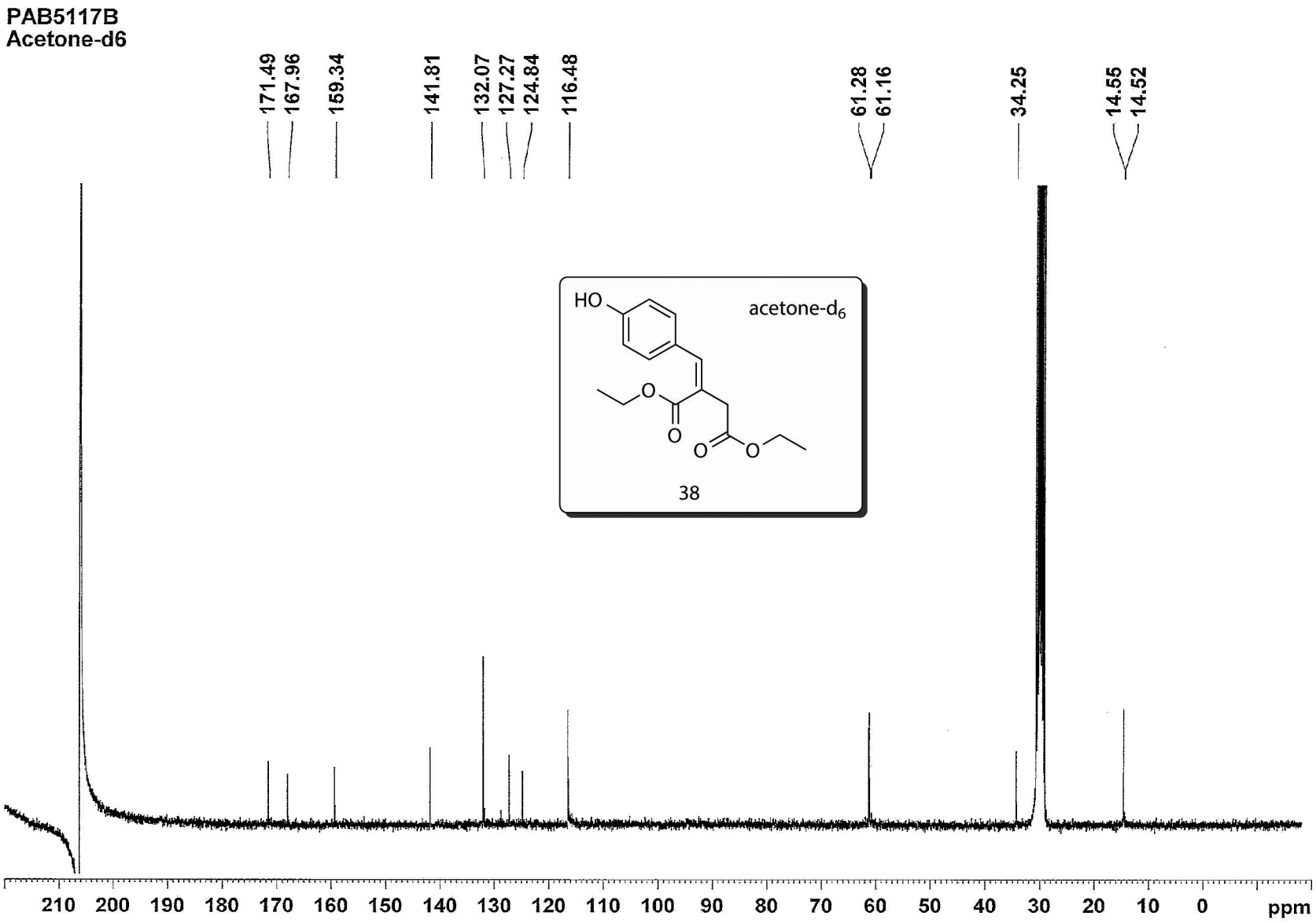
PAB5095A


7.832
7.341
7.311
6.924
6.919
6.895
4.298
4.274
4.270
4.251
4.246
4.227
4.221
4.197
4.173
4.162
4.149
3.818
3.549
1.347
1.323
1.318
1.299
1.288
1.264
1.259
1.240
MeO
O
O
O
O
37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.00
2.03
4.26
3.15
2.00
6.82

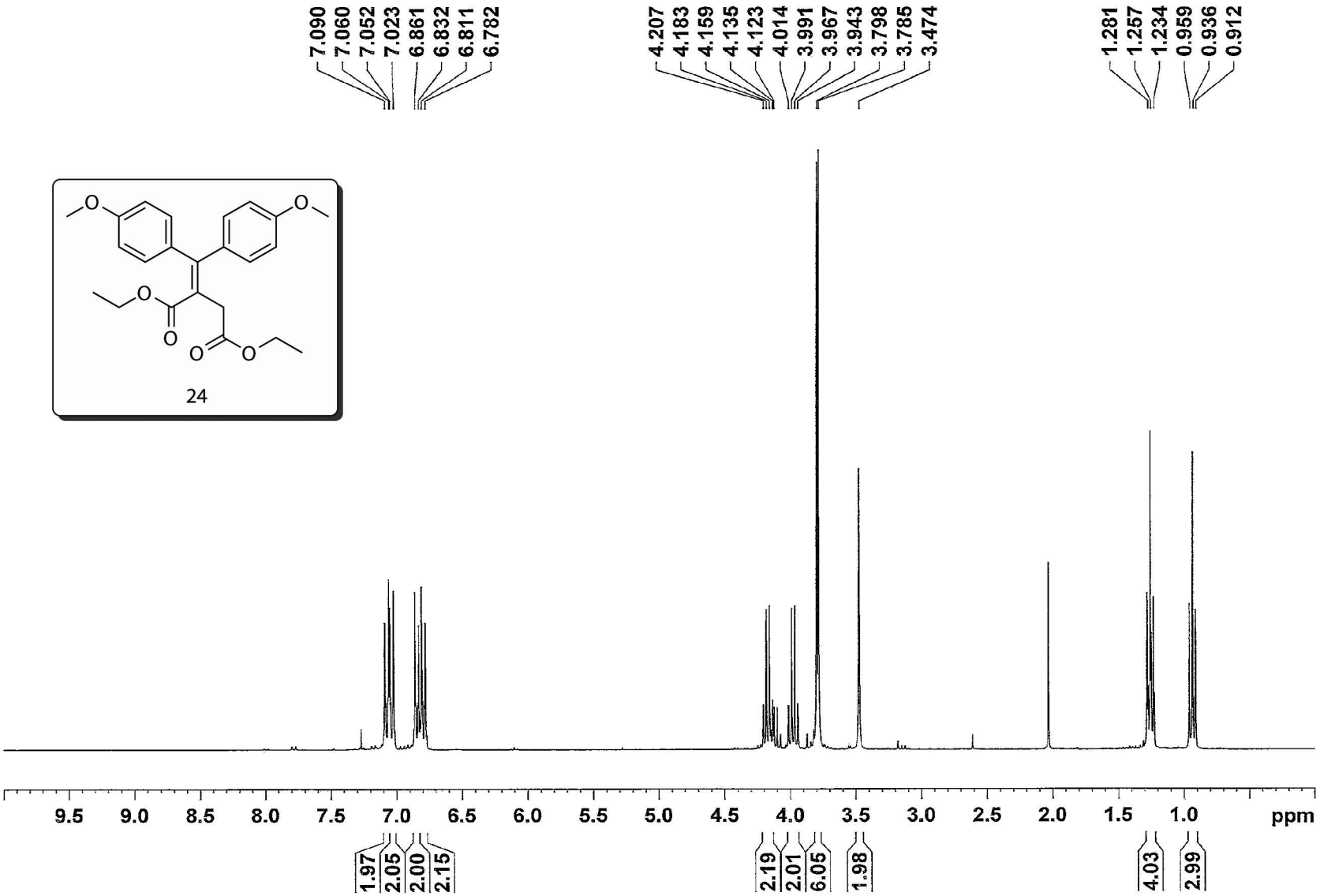
PAB5095A


171.21
167.52
160.08
141.31
130.78
127.40
124.19
113.98
60.88
60.79
55.19
33.67
14.15
14.09
MeO
O
O
O
O
37
200
180
160
140
120
100
80
60
40
20
0
ppm

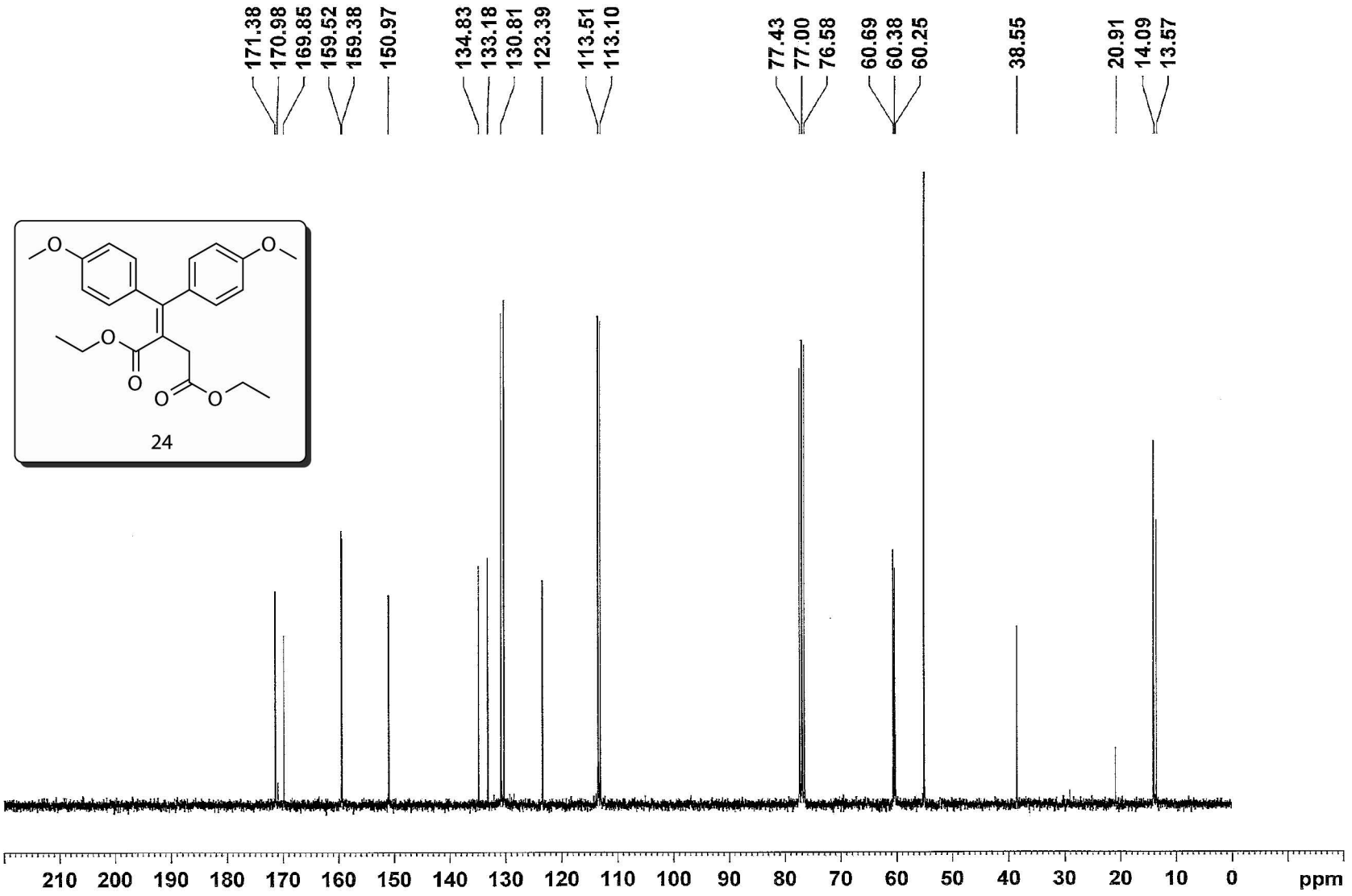

PAB5117D
Acetone-d6
8.776
7.774
7.354
7.325
6.922
6.893
4.250
4.226
4.202
4.178
4.152
4.129
4.105
3.543
1.310
1.287
1.263
1.253
1.229
1.206
HO
acetone-d6
O
O
O
O
38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.63
0.90
2.00
2.01
4.18
1.89
6.39


PAB5117B
Acetone-d6
171.49
167.96
159.34
141.81
132.07
127.27
124.84
116.48
61.28
61.16
34.25
14.55
14.52
HO
acetone-d6
O
O
O
O
38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

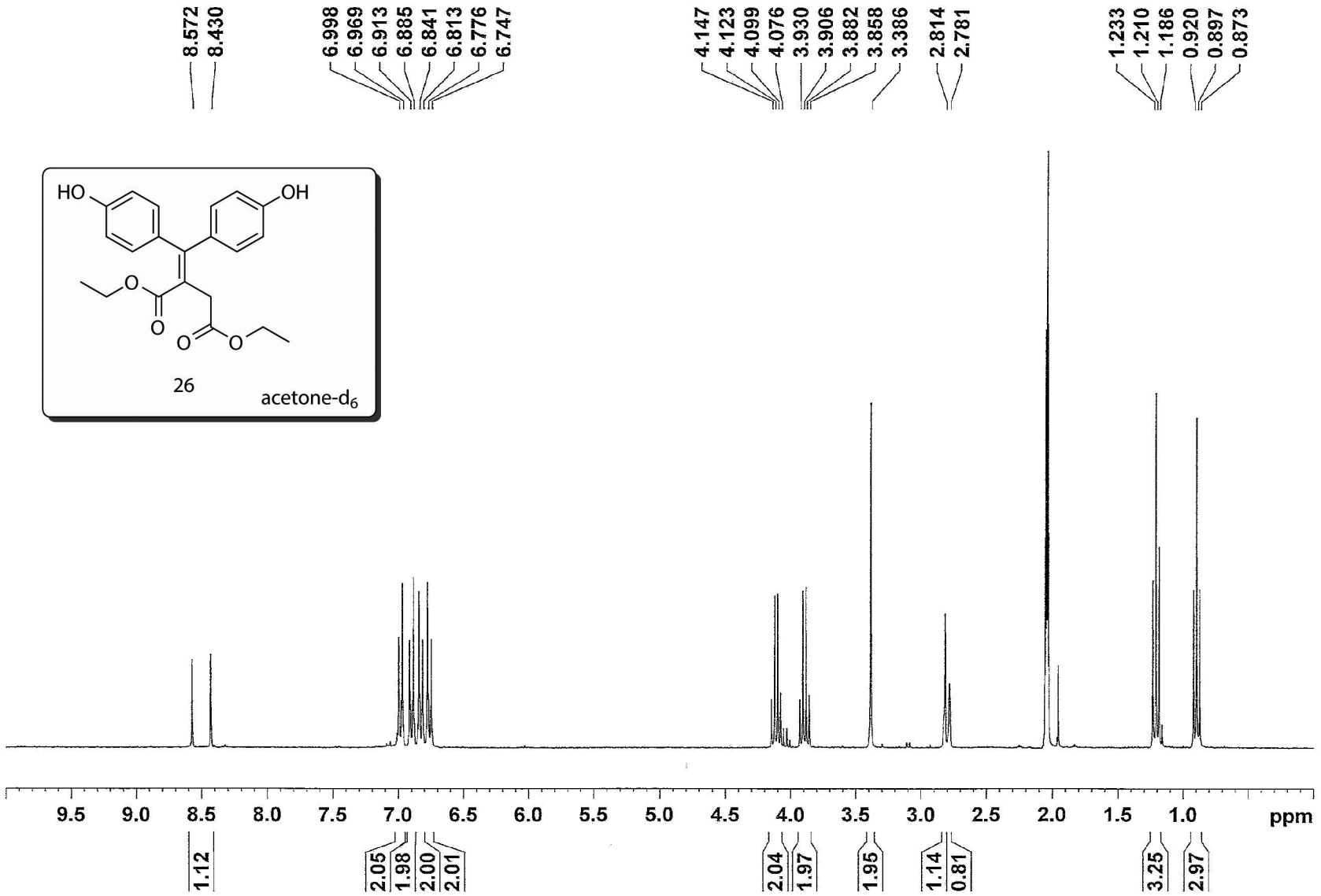
PAB5155B

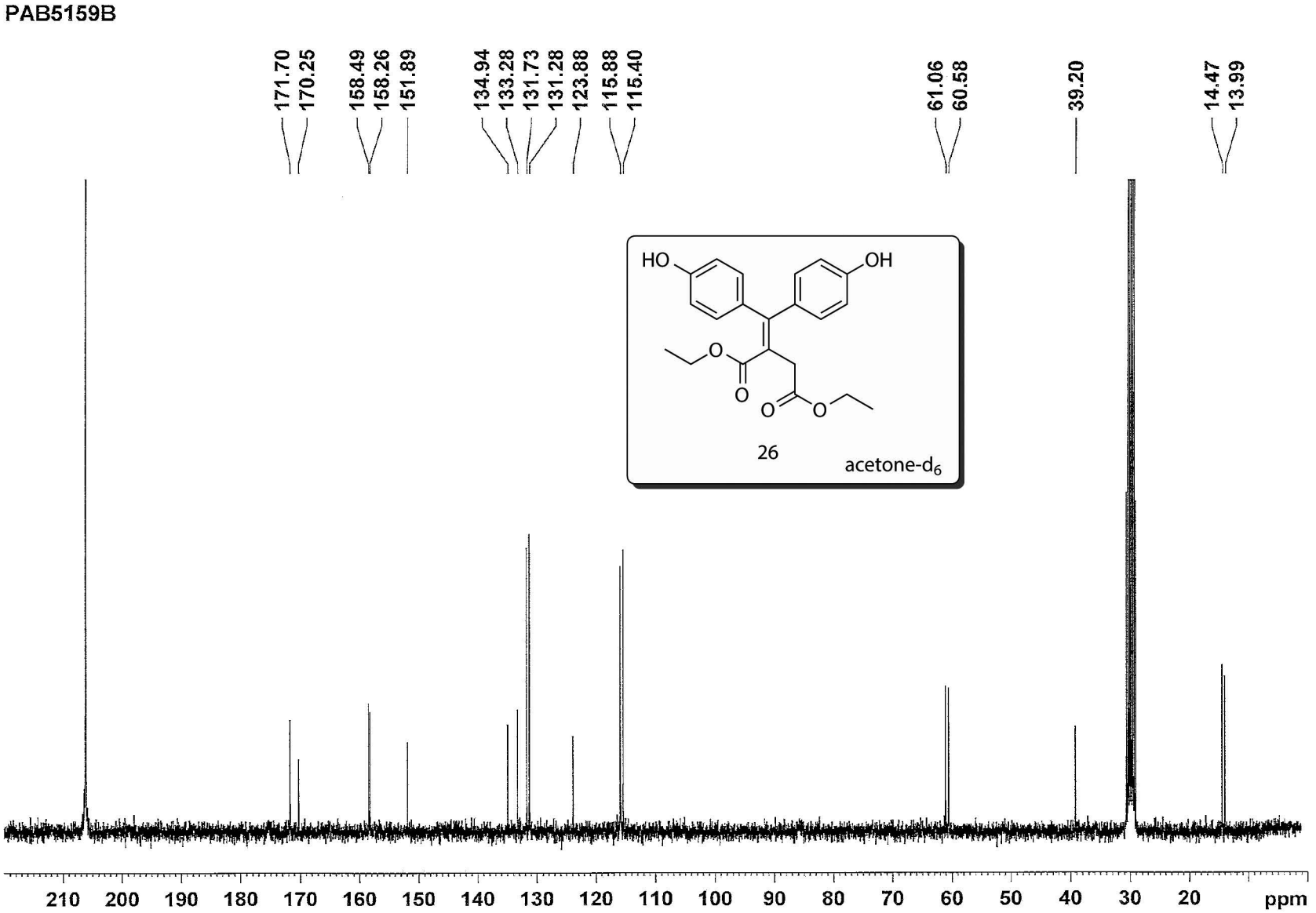

7.090
7.060
7.052
7.023
6.861
6.832
6.811
6.782
4.207
4.183
4.159
4.135
4.123
4.014
3.991
3.967
3.943
3.798
3.785
3.474
1.281
1.257
1.234
0.959
0.936
0.912
24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.97
2.05
2.00
2.15
2.19
2.01
6.05
1.98
4.03
2.99

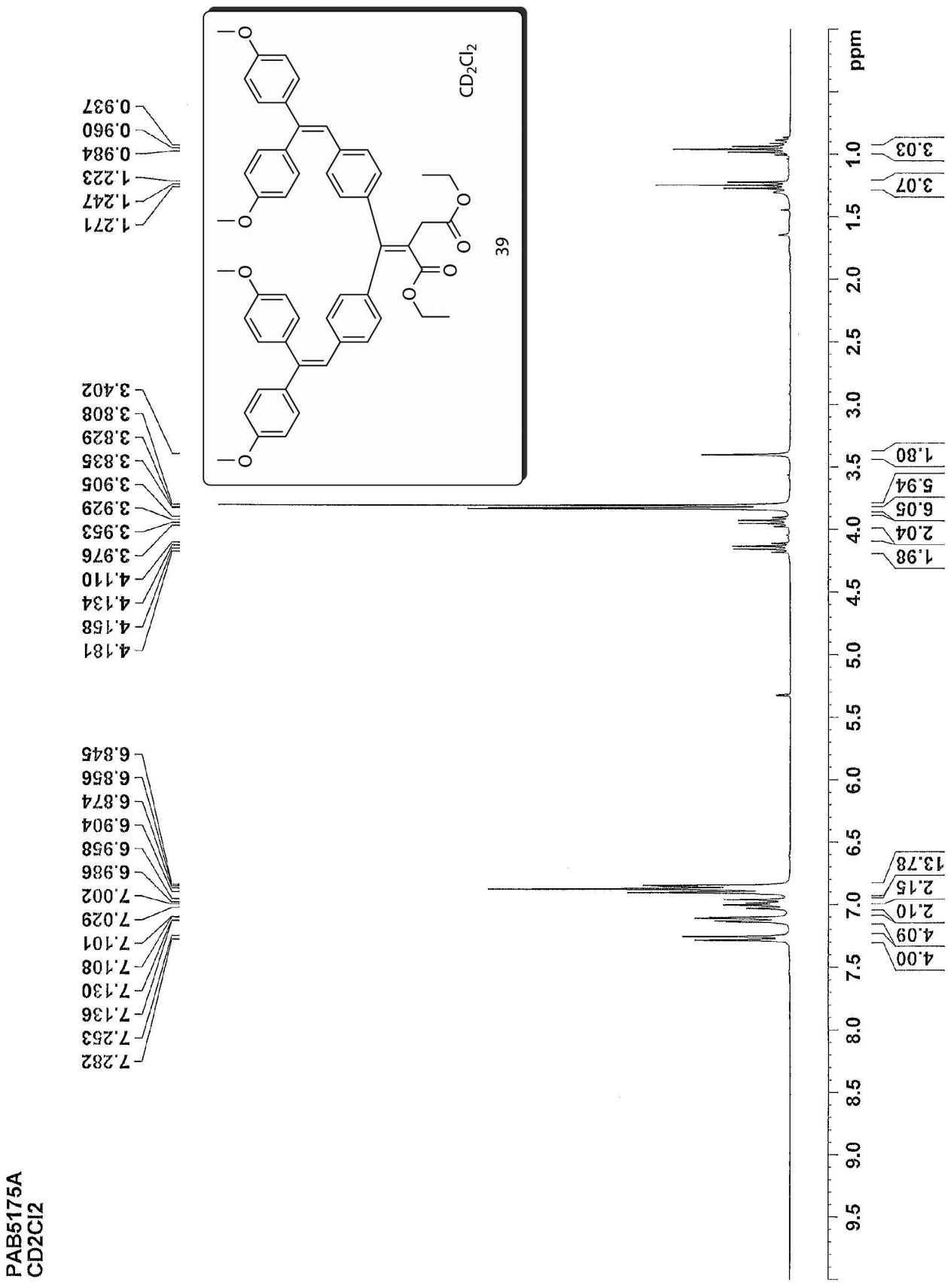
PAB5155B


171.38
170.98
169.85
159.52
159.38
150.97
134.83
133.18
130.81
123.39
113.51
113.10
77.43
77.00
76.58
60.69
60.38
60.25
38.55
20.91
14.09
13.57
O
O
O
O
O
O
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

PAB5159A


8.572
8.430
6.998
6.969
6.913
6.885
6.841
6.813
6.776
6.747
4.147
4.123
4.099
4.076
3.930
3.906
3.882
3.858
3.386
2.814
2.781
1.233
1.210
1.186
0.920
0.897
0.873
HO
OH
O
O
O
O
26
acetone-d6
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.12
2.05
1.98
2.00
2.01
2.04
1.97
1.95
1.14
0.81
3.25
2.97


PAB5159B
171.70
170.25
158.49
158.26
151.89
134.94
133.28
131.73
131.28
123.88
115.88
115.40
61.06
60.58
39.20
14.47
13.99
HO
OH
O
O
O
O
26
acetone-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
4.00
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2.10
2.15
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6.874
6.904
6.958
6.986
7.002
7.029
7.101
7.108
7.130
7.136
7.253
7.282
1.98
2.04
6.05
5.94
1.80
4.181
4.158
4.134
4.110
3.976
3.953
3.929
3.905
3.835
3.829
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3.07
3.03
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1.247
1.223
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0.960
0.937

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136.45
133.00
132.85
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129.21
129.17
129.11
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125.92
125.67
125.30
114.42
113.90
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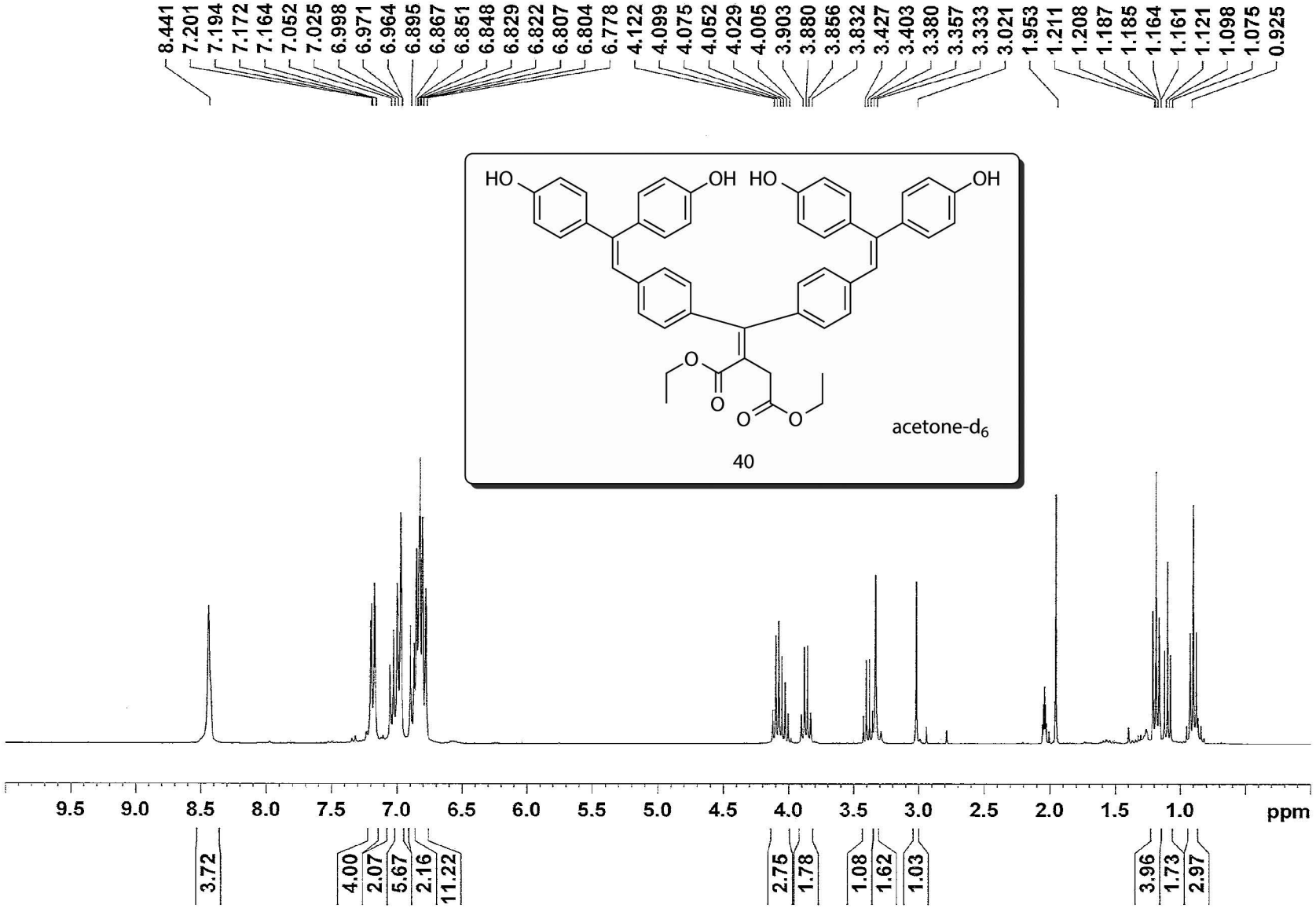
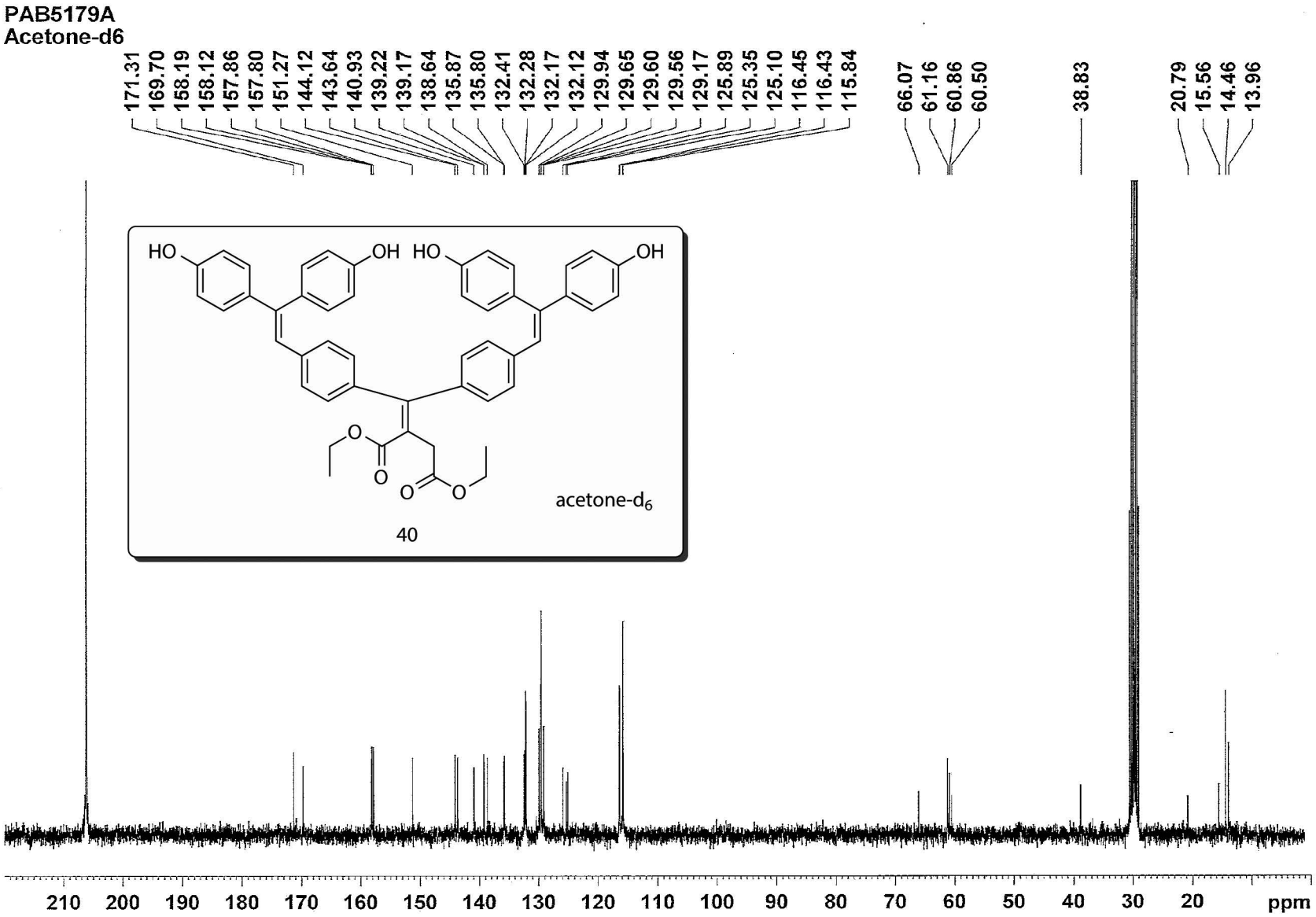
CD2Cl2
39
ppm

PAB5179A
Acetone-d6

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139.22
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135.87
135.80
132.41
132.28
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132.12
129.94
129.65
129.60
129.56
129.17
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125.35
125.10
116.45
116.43
115.84
66.07
61.16
60.86
60.50
38.83
20.79
15.56
14.46
13.96
HO
OH
HO
OH
O
O
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40
210
200
190
180
170
160
150
140
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110
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40
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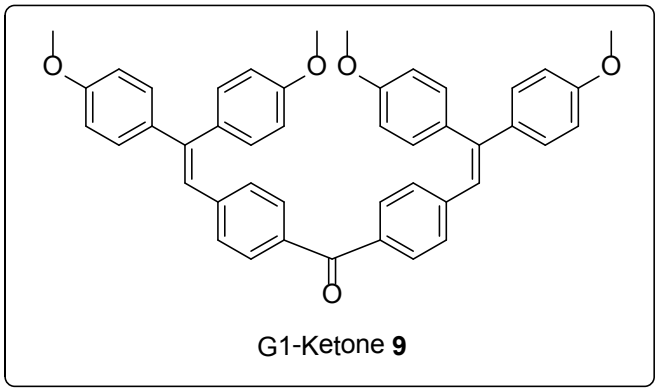
APPENDIX B

X-RAY CRYSTAL DATA FOR G1-KETONE 9



This appendix contains the tables of data related to the x-ray crystal structure of G1-Ketone **9**.

Following those tables are figures showing the structure of the compound from various angles compared with the minimized equilibrium geometry as calculated using B3LYP/STO-3G methods[152] with GAMESS.[89]

Table B.1. Crystal data and structure refinement for **9**.

Identification code	pb0701t	
Empirical formula	$C_{45}H_{38}O_5$	
Formula weight	658.75	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 35.5065(16) Å	α= 90°.
	b = 12.6761(6) Å	β= 90°.
	c = 8.1714(4) Å	γ = 90°.
Volume	3677.8(3) $Å^3$	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	1392	
Crystal size	0.15 x 0.15 x 0.35 mm^3	
Theta range for data collection	1.71 to 25.00°	
Index ranges	-42<=h<=42, -15<=k<=15, -9<=l<=9	
Reflections collected	27564	
Independent reflections	3235 [R(int) = 0.0445]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3235 / 0 / 227	
Goodness-of-fit on F^2	1.346	
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1575	
R indices (all data)	R1 = 0.0823, wR2 = 0.1663	
Largest diff. peak and hole	0.166 and -0.148 $e.Å^{-3}$	

Table B.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	0	12872(2)	2500	111(1)
O(2)	703(1)	5350(1)	2093(2)	84(1)
O(3)	3171(1)	8223(2)	1870(3)	100(1)
C(1)	783(1)	9880(2)	2786(3)	55(1)
C(2)	435(1)	10336(2)	2930(3)	54(1)
C(3)	364(1)	11342(2)	2306(3)	54(1)
C(4)	661(1)	11866(2)	1561(3)	59(1)
C(5)	1009(1)	11413(2)	1435(3)	58(1)
C(6)	1082(1)	10401(2)	2022(3)	52(1)
C(7)	0	11905(2)	2500	64(1)
C(8)	1467(1)	10000(2)	1883(3)	61(1)
C(9)	1606(1)	9011(2)	1916(3)	59(1)
C(10)	1366(1)	8056(2)	1912(3)	52(1)
C(11)	1083(1)	7904(2)	774(3)	58(1)
C(12)	856(1)	7020(2)	785(3)	61(1)
C(13)	908(1)	6261(2)	1965(3)	59(1)
C(14)	1188(1)	6394(2)	3119(3)	65(1)
C(15)	1418(1)	7264(2)	3070(3)	59(1)
C(16)	400(1)	5203(2)	996(4)	87(1)
C(17)	2018(1)	8832(2)	1931(3)	62(1)
C(18)	2263(1)	9488(2)	2768(3)	71(1)
C(19)	2649(1)	9323(2)	2768(3)	76(1)
C(20)	2795(1)	8479(2)	1920(3)	73(1)
C(21)	2558(1)	7819(2)	1079(4)	88(1)
C(22)	2178(1)	7989(2)	1104(3)	79(1)
C(23)	3426(1)	8907(3)	2627(5)	101(1)

Table B.3. Bond lengths [Å] and angles [°] for **9**.

O(1)-C(7)	1.226(4)
O(2)-C(13)	1.369(3)
O(2)-C(16)	1.411(3)
O(3)-C(20)	1.375(3)
O(3)-C(23)	1.398(3)
C(1)-C(2)	1.370(3)
C(1)-C(6)	1.399(3)
C(1)-H(1A)	0.9300
C(2)-C(3)	1.396(3)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.388(3)
C(3)-C(7)	1.484(3)
C(4)-C(5)	1.367(3)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.394(3)
C(5)-H(5A)	0.9300
C(6)-C(8)	1.461(3)
C(7)-C(3)#1	1.484(3)
C(8)-C(9)	1.348(3)
C(8)-H(8A)	0.9300
C(9)-C(10)	1.480(3)
C(9)-C(17)	1.479(3)
C(10)-C(11)	1.383(3)
C(10)-C(15)	1.392(3)
C(11)-C(12)	1.380(3)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.374(3)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.382(3)
C(14)-C(15)	1.373(3)
C(14)-H(14A)	0.9300
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.9600

Table B.3. (continued)

C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-C(18)	1.384(3)
C(17)-C(22)	1.386(3)
C(18)-C(19)	1.386(3)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.376(4)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.371(4)
C(21)-C(22)	1.370(4)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

C(13)-O(2)-C(16)	117.9(2)
C(20)-O(3)-C(23)	118.0(2)
C(2)-C(1)-C(6)	121.7(2)
C(2)-C(1)-H(1A)	119.2
C(6)-C(1)-H(1A)	119.2
C(1)-C(2)-C(3)	121.1(2)
C(1)-C(2)-H(2A)	119.4
C(3)-C(2)-H(2A)	119.4
C(4)-C(3)-C(2)	117.4(2)
C(4)-C(3)-C(7)	118.6(2)
C(2)-C(3)-C(7)	123.9(2)
C(5)-C(4)-C(3)	121.2(2)
C(5)-C(4)-H(4A)	119.4
C(3)-C(4)-H(4A)	119.4
C(4)-C(5)-C(6)	122.0(2)
C(4)-C(5)-H(5A)	119.0

Table B.3. (continued)

C(6)-C(5)-H(5A)	119.0
C(5)-C(6)-C(1)	116.5(2)
C(5)-C(6)-C(8)	117.9(2)
C(1)-C(6)-C(8)	125.5(2)
O(1)-C(7)-C(3)	118.74(13)
O(1)-C(7)-C(3)#1	118.74(13)
C(3)-C(7)-C(3)#1	122.5(3)
C(9)-C(8)-C(6)	131.6(2)
C(9)-C(8)-H(8A)	114.2
C(6)-C(8)-H(8A)	114.2
C(8)-C(9)-C(10)	123.3(2)
C(8)-C(9)-C(17)	120.3(2)
C(10)-C(9)-C(17)	116.38(19)
C(11)-C(10)-C(15)	117.0(2)
C(11)-C(10)-C(9)	122.3(2)
C(15)-C(10)-C(9)	120.73(19)
C(12)-C(11)-C(10)	122.2(2)
C(12)-C(11)-H(11A)	118.9
C(10)-C(11)-H(11A)	118.9
C(13)-C(12)-C(11)	119.6(2)
C(13)-C(12)-H(12A)	120.2
C(11)-C(12)-H(12A)	120.2
O(2)-C(13)-C(12)	124.9(2)
O(2)-C(13)-C(14)	115.7(2)
C(12)-C(13)-C(14)	119.4(2)
C(15)-C(14)-C(13)	120.4(2)
C(15)-C(14)-H(14A)	119.8
C(13)-C(14)-H(14A)	119.8
C(14)-C(15)-C(10)	121.3(2)
C(14)-C(15)-H(15A)	119.3
C(10)-C(15)-H(15A)	119.3
O(2)-C(16)-H(16A)	109.5
O(2)-C(16)-H(16B)	109.5

Table B.3. (continued)

H(16A)-C(16)-H(16B)	109.5
O(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	116.5(2)
C(18)-C(17)-C(9)	122.3(2)
C(22)-C(17)-C(9)	121.2(2)
C(19)-C(18)-C(17)	122.1(2)
C(19)-C(18)-H(18A)	119.0
C(17)-C(18)-H(18A)	119.0
C(20)-C(19)-C(18)	119.4(2)
C(20)-C(19)-H(19A)	120.3
C(18)-C(19)-H(19A)	120.3
C(21)-C(20)-C(19)	119.7(2)
C(21)-C(20)-O(3)	115.8(2)
C(19)-C(20)-O(3)	124.4(2)
C(22)-C(21)-C(20)	120.1(2)
C(22)-C(21)-H(21A)	120.0
C(20)-C(21)-H(21A)	120.0
C(21)-C(22)-C(17)	122.2(2)
C(21)-C(22)-H(22A)	118.9
C(17)-C(22)-H(22A)	118.9
O(3)-C(23)-H(23A)	109.5
O(3)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(3)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table B.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	87(2)	43(2)	203(3)	0	36(2)	0
O(2)	96(1)	70(1)	85(1)	11(1)	-8(1)	-26(1)
O(3)	53(1)	116(2)	129(2)	-40(1)	5(1)	-5(1)
C(1)	59(1)	48(1)	57(1)	6(1)	-4(1)	-1(1)
C(2)	55(1)	52(1)	56(1)	2(1)	-1(1)	-8(1)
C(3)	60(1)	43(1)	58(1)	-2(1)	-3(1)	-4(1)
C(4)	70(2)	41(1)	66(1)	2(1)	0(1)	-5(1)
C(5)	62(2)	49(1)	64(1)	-3(1)	8(1)	-10(1)
C(6)	55(1)	48(1)	54(1)	-4(1)	-2(1)	-7(1)
C(7)	68(2)	42(2)	81(2)	0	3(2)	0
C(8)	56(1)	60(1)	69(2)	-2(1)	2(1)	-11(1)
C(9)	57(1)	59(1)	61(1)	-7(1)	-2(1)	-3(1)
C(10)	48(1)	54(1)	56(1)	-6(1)	0(1)	5(1)
C(11)	63(1)	57(1)	54(1)	6(1)	-6(1)	-6(1)
C(12)	59(1)	65(1)	58(1)	0(1)	-10(1)	-7(1)
C(13)	65(2)	53(1)	58(1)	0(1)	4(1)	-4(1)
C(14)	74(2)	56(1)	64(1)	7(1)	-7(1)	6(1)
C(15)	55(1)	59(1)	62(1)	-7(1)	-9(1)	12(1)
C(16)	86(2)	84(2)	91(2)	-9(2)	-1(2)	-31(2)
C(17)	58(2)	63(1)	66(1)	-12(1)	1(1)	-5(1)
C(18)	62(2)	66(2)	84(2)	-17(1)	-3(1)	0(1)
C(19)	63(2)	77(2)	88(2)	-19(1)	-9(1)	-12(1)
C(20)	52(2)	84(2)	83(2)	-20(1)	8(1)	-7(1)
C(21)	57(2)	95(2)	112(2)	-46(2)	11(1)	-3(2)
C(22)	57(2)	92(2)	89(2)	-39(2)	3(1)	-10(1)
C(23)	59(2)	120(3)	126(3)	-19(2)	-9(2)	-19(2)

Table B.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **9**.

	x	y	z	U(eq)
H(1A)	821	9207	3208	65
H(2A)	242	9969	3453	65
H(4A)	623	12539	1139	71
H(5A)	1203	11791	943	70
H(8A)	1648	10521	1747	74
H(11A)	1044	8414	-26	70
H(12A)	669	6938	-1	73
H(14A)	1222	5890	3933	77
H(15A)	1613	7326	3825	71
H(16A)	281	4538	1216	130
H(16B)	493	5209	-107	130
H(16C)	221	5762	1134	130
H(18A)	2166	10057	3348	85
H(19A)	2807	9779	3335	91
H(21A)	2657	7254	490	106
H(22A)	2021	7524	546	95
H(23A)	3677	8637	2502	152
H(23B)	3367	8962	3770	152
H(23C)	3410	9591	2129	152

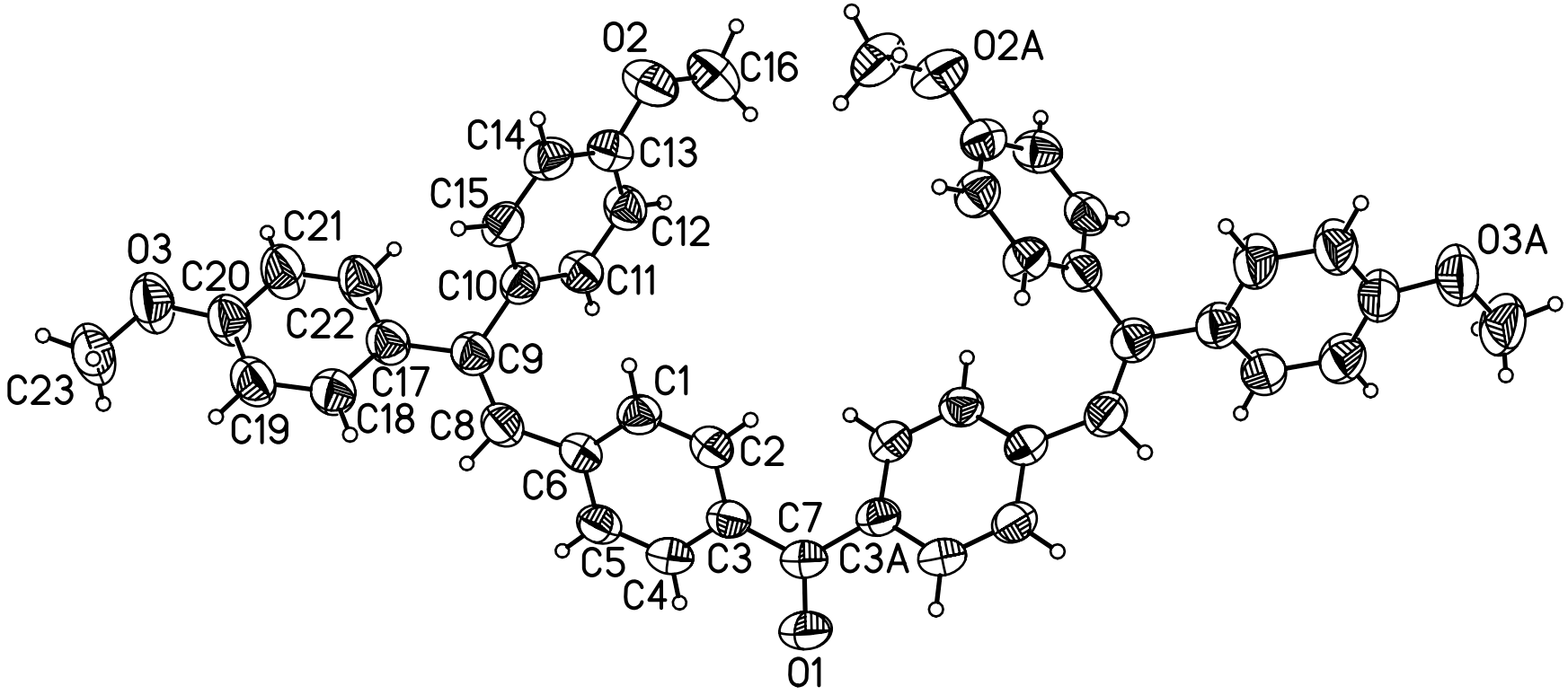


Figure B.1. ORTEP diagram from crystal structure of G1-Ketone **9** with atom assignments.

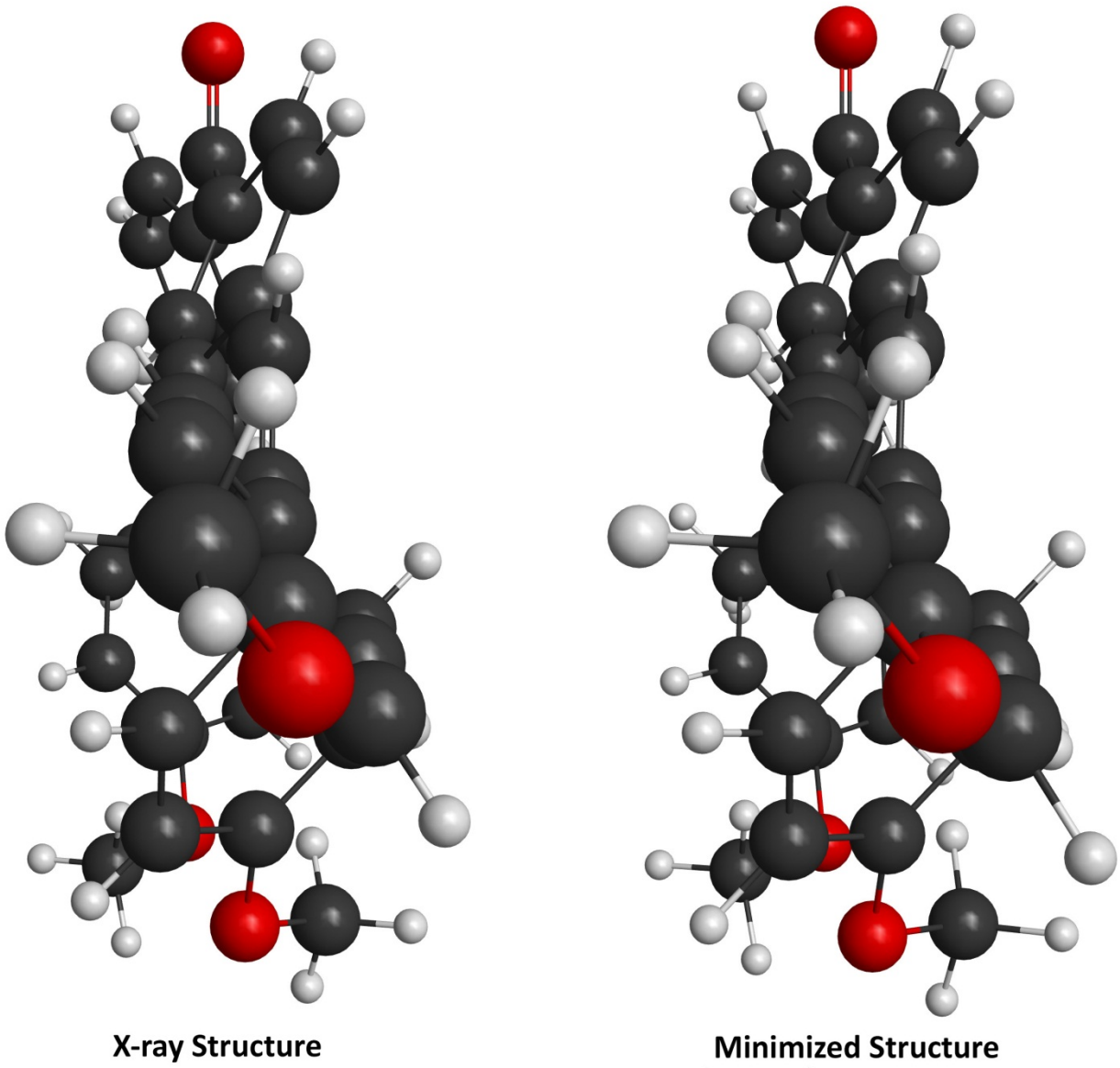


Figure B.2. Comparison of structures of G1-Ketone as viewed from x-axis.

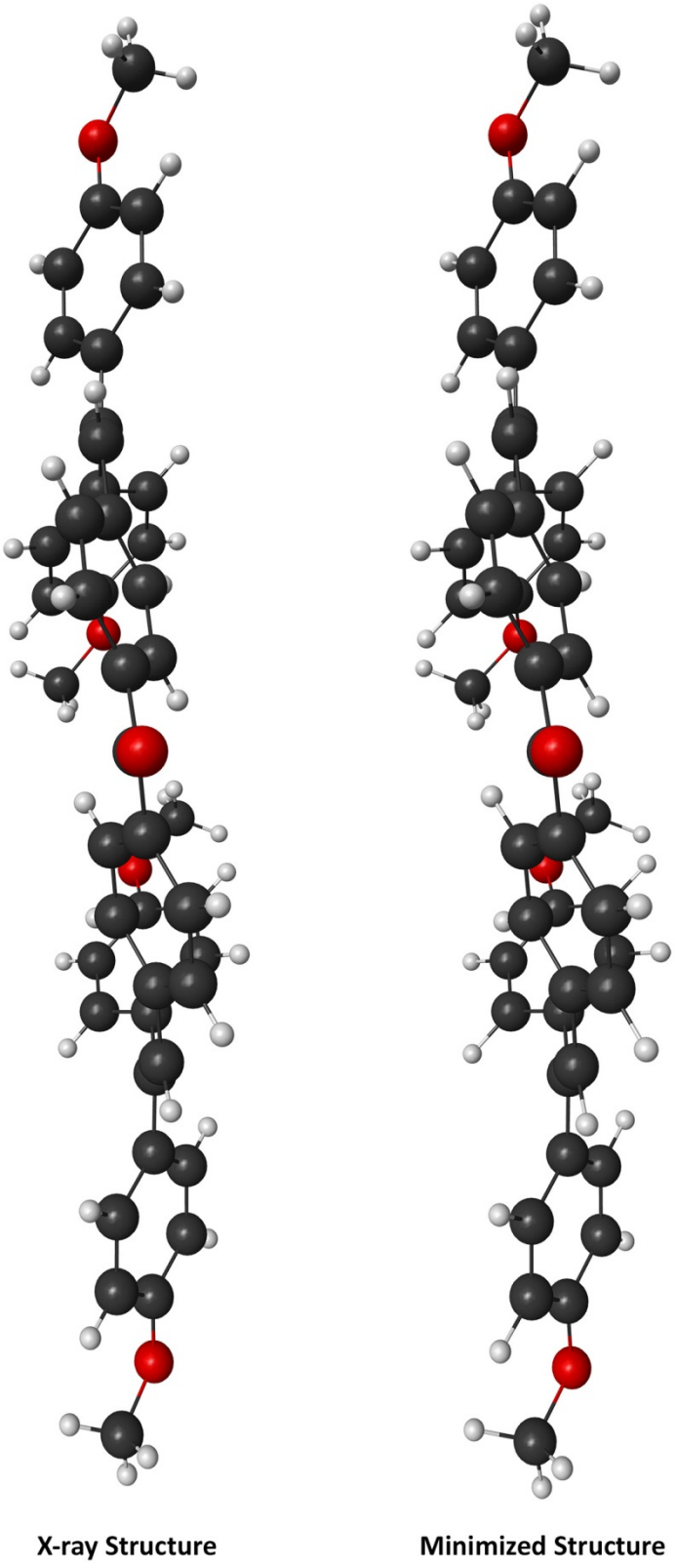


Figure B.3. Comparison of structures of G1-Ketone as viewed from y-axis.

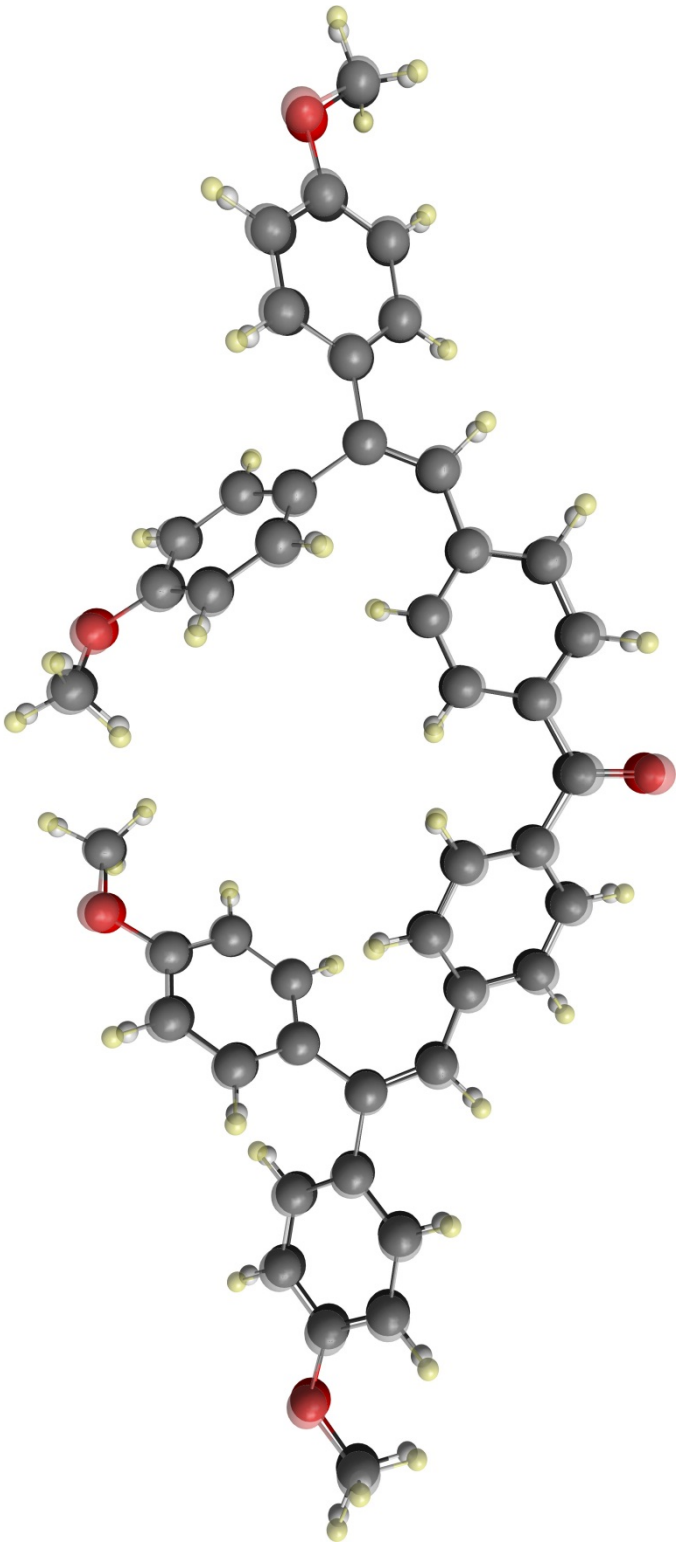


Figure B.4. Comparison of structures of G1-Ketone as viewed from z-axis. X-ray structure in back with minimized structure over top with decreased opacity.

APPENDIX C

ADDITIONAL UV-VISIBLE ABSORPTION AND FLUORESCENCE DATA FOR PHENYLENE VINYLENE DENDRONS

Experimental Conditions

Solvent: dichloromethane

Solution Concentrations:

G0-Ketone **7**	1.4×10^{-5} M
G1-Ketone **9**	5.3×10^{-6} M
G1-Acetal **8**	5.2×10^{-6} M
G2-Acetal **10**	5.5×10^{-6} M
G0-OTBS **16**	5.6×10^{-6} M
G1-OTBS **19**	5.3×10^{-6} M

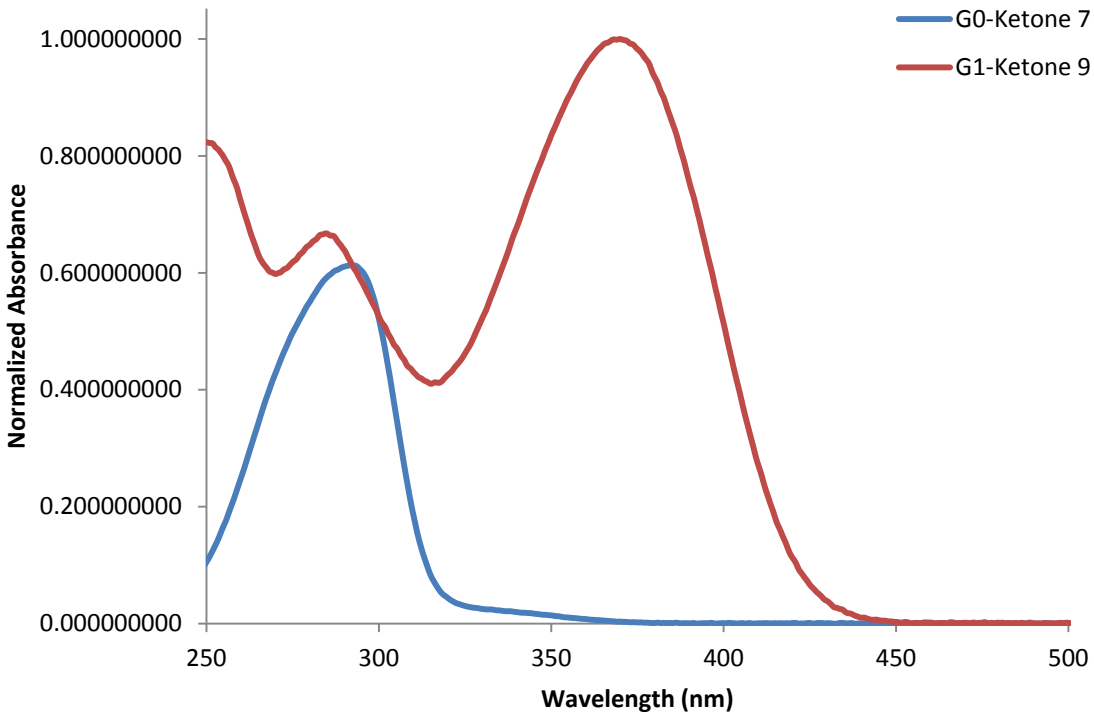


Figure C.1. UV-visible absorption spectra of G0- & G1-Ketone dendrons adjusted to reflect a common concentration and normalized.

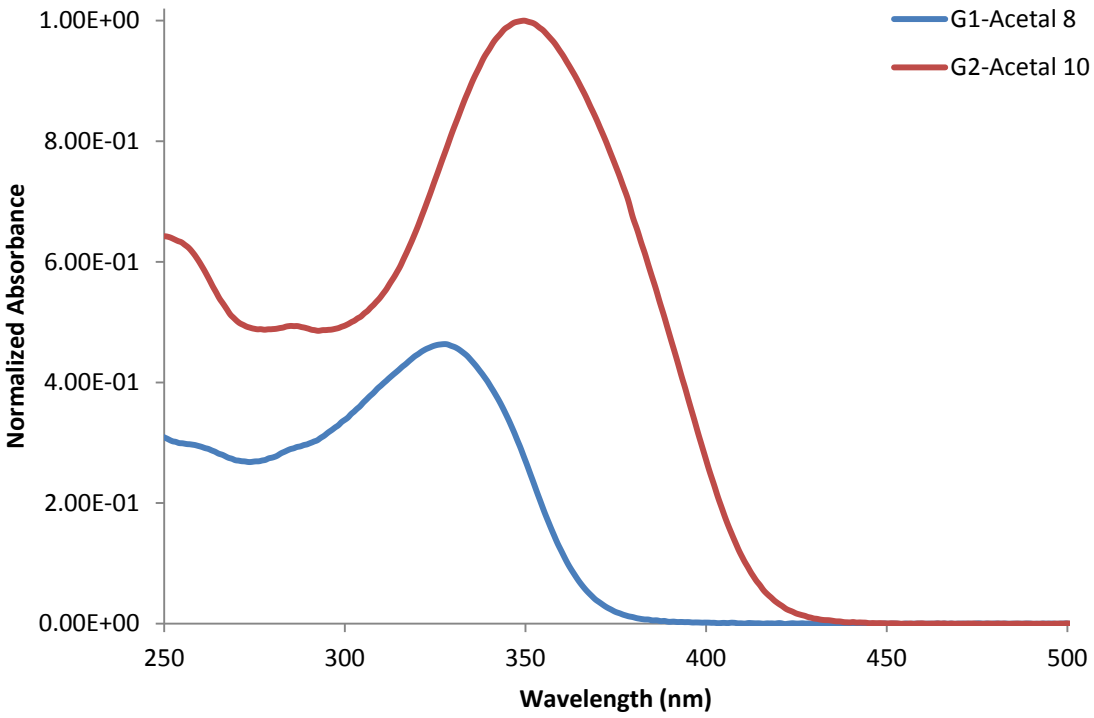


Figure C.2. UV-visible absorption spectra of G1- & G2-Acetal dendrons adjusted to reflect a common concentration and normalized.

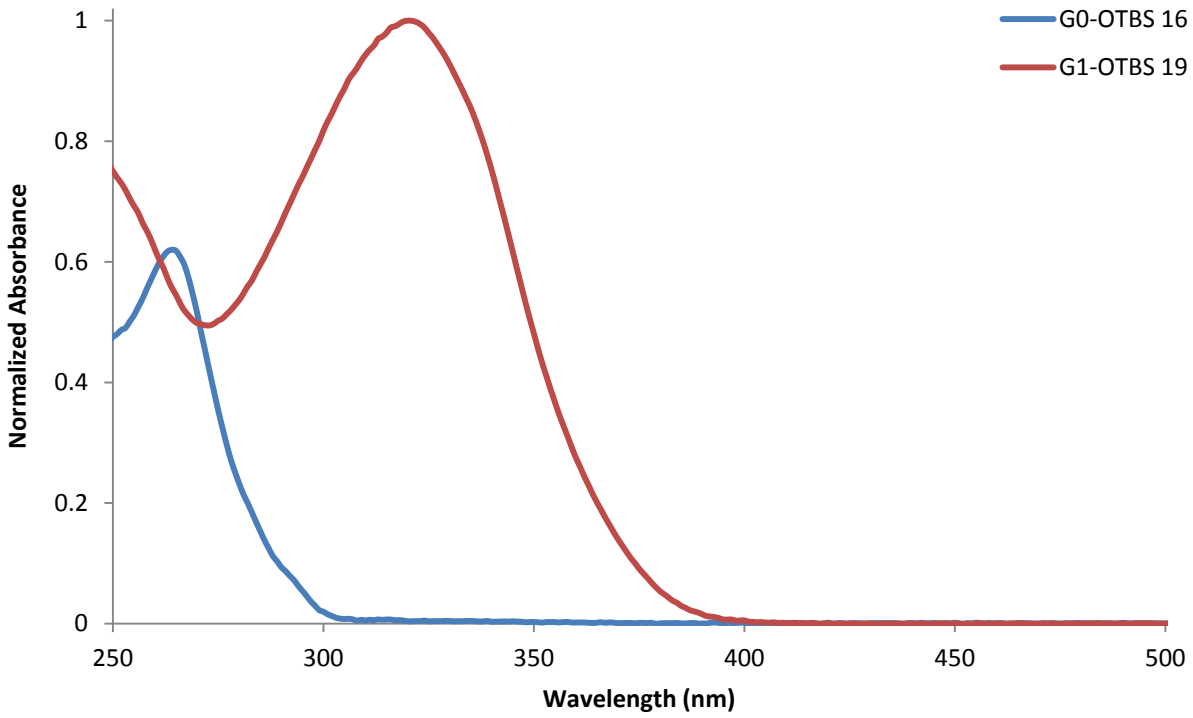


Figure C.3. UV-visible absorption spectra of G0- & G1-OTBS dendrons adjusted to reflect a common concentration and normalized.

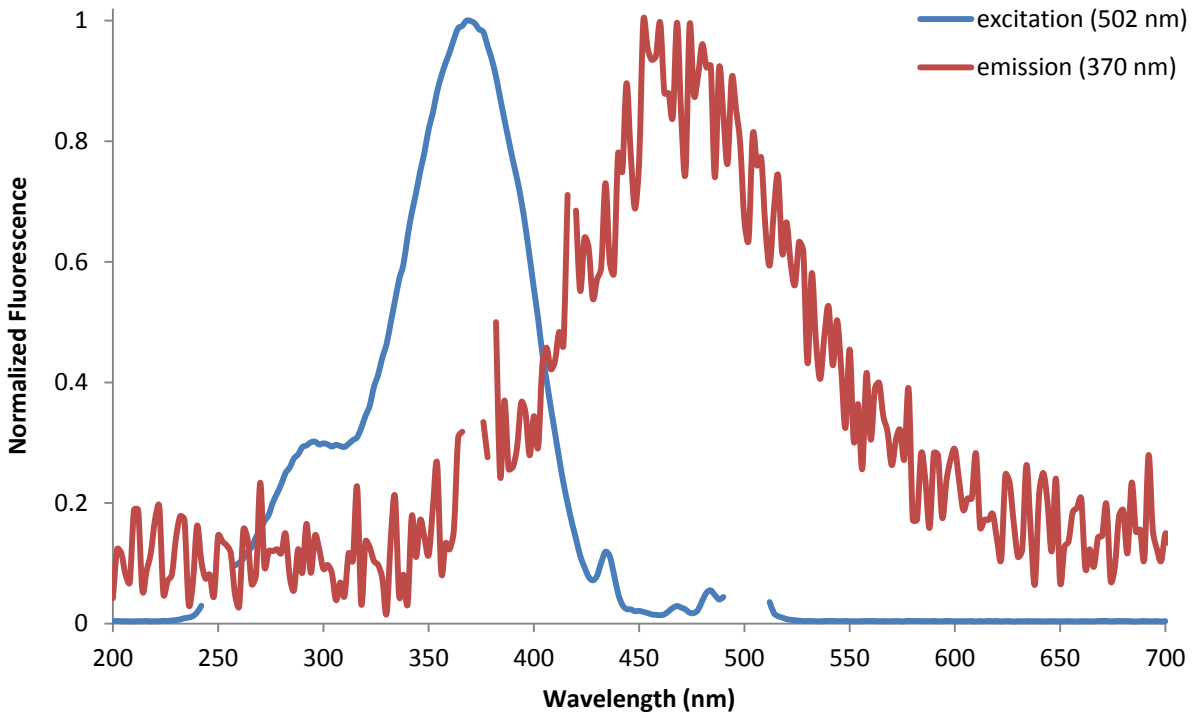


Figure C.4. Fluorescence excitation and emission spectra of G1-Ketone dendron.

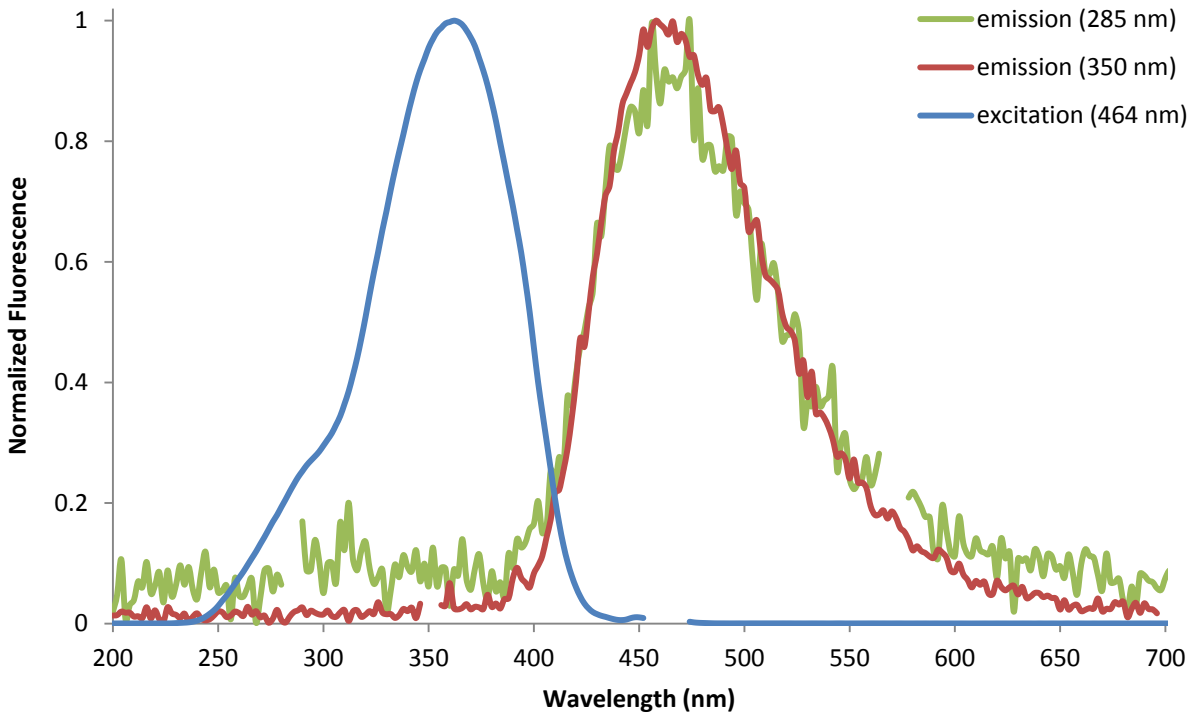


Figure C.5. Fluorescence excitation and emission spectra of G2-Acetal dendron.

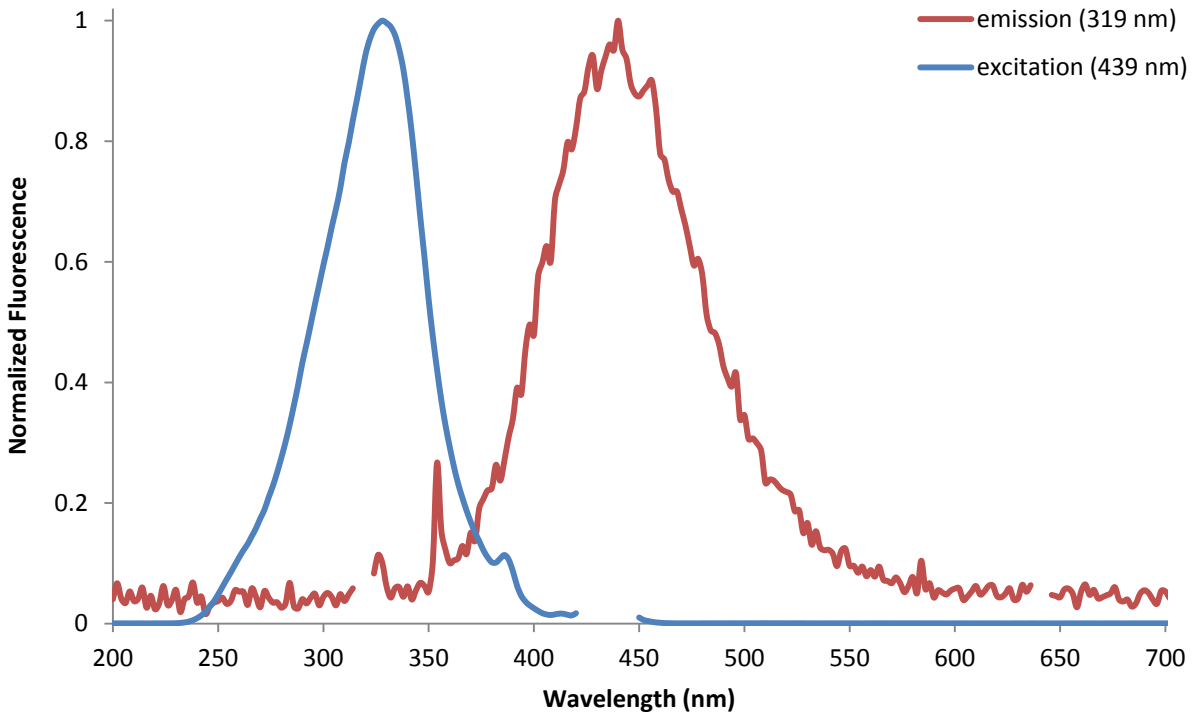


Figure C.6. Fluorescence excitation and emission spectra of G1-OTBS dendron.

APPENDIX D

ADDITIONAL FLUORESCENCE DATA FOR DYES

Experimental Conditions

Solvent: dichloromethane

Solution Concentrations:

Ni-Por **29**	1.4×10^{-6} M
1P-Dye **33**	3.8×10^{-6} M
2P-Dye **34**	4.7×10^{-6} M
4P-Dye **35**	2.7×10^{-6} M

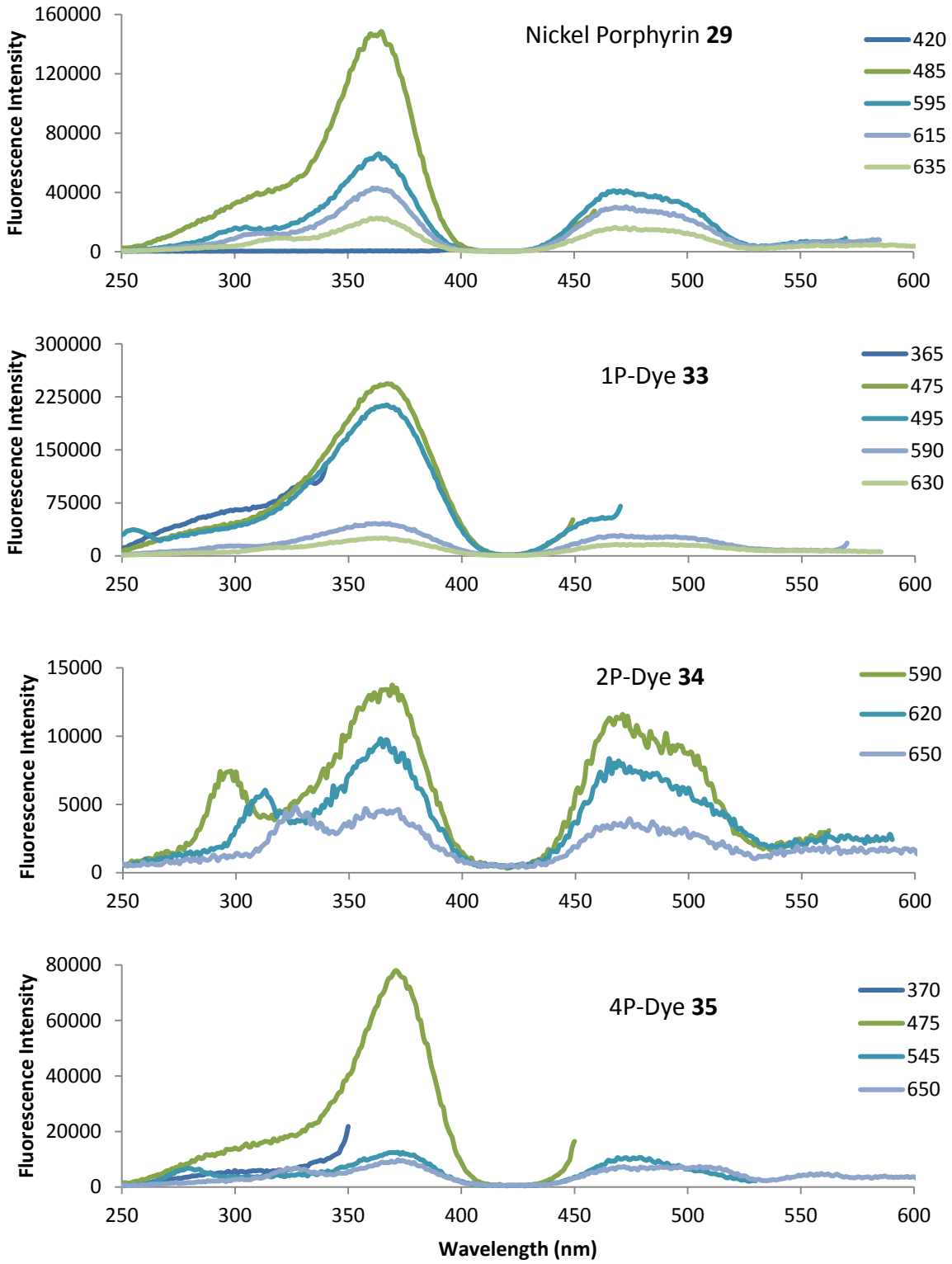


Figure D.1. Fluorescence excitation spectra as recorded of porphyrin **29** and dyes **33-35** as observed at wavelengths shown in legends.

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